13th Canadian Symposium
on
Theoretical Chemistry

The University of British Columbia
Vancouver, Canada
August 2 - 7, 1998

Program and Abstracts

Sponsored by the
Canadian Association of Theoretical Chemists

Welcome

Welcome to Vancouver and The University of British Columbia!

This book was sent to press on the morning of July 13, 1998. Therefore abstracts and registrations received after that time do not appear in this book.

We are very pleased to acknowledge the financial assistance of

The Department of Chemistry, University of British Columbia

The Faculty of Science, University of British Columbia

The Vice President Research, University of British Columbia

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We are also very grateful for the assistance of Rowena Tate and the University of British Columbia Conference Centre. The symposium would not have been possible without their excellent organizational support.

Finally, we wish you an enjoyable visit and a successful meeting.

Tom Ziegler
Department of Chemistry
University of Calgary
Calgary, Alberta
Canada, T2N 1N4

Gren Patey
Department of Chemistry
University of British Columbia
Vancouver, B.C.
Canada, V6T 1Z1

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General Information

Badge

Admission to all conference activities is by name badge, so please be sure to wear your badge at all times. Please help us recycle by returning your name badge holder to the Registration Desk when you leave the conference for the final time.

Banking and Foreign Exchange

Canadian and American currency (cash or travellers' cheques) are accepted by business establishments. Other currencies can be exchanged at banks only. All major credit cards are widely accepted in Vancouver. Visa and MasterCard are accepted for University accommodation and conference registration fees.

The Bank of Montreal, in the basement of the Student Union Building (SUB), is open 10:00–16:00 Monday to Thursday, 10:00–17:00 Friday. The Canadian Imperial Bank of Commerce, in the University Village, is open 09:30–16:30 Monday to Thursday, 09:30–17:00 Friday. Both banks have 24 hour automated teller machines (ATMs). ATMs are also located in the lobby of the Walter Gage Residence and the Student Union Building.

Dining

The Pacific Spirit Place Cafeteria, located in the Student Union Building (SUB), is open from 07:00–14:30 for breakfast and lunch, and from 16:30–19:00 for dinner seven days a week. There are also numerous other food outlets in SUB and the University Village. Pick up information on these and restaurants in Vancouver from the Tourism Table at the Registration Desk.

E-mail

You can access your e-mail at "To The Letter" located in the Student Union Building basement. Open Monday to Friday 10:00–17:00, phone 822-5640.

Emergency Telephone Numbers

Emergency Centre	911
Ambulance	872-5151
Fire	822-4567
Police (RCMP)	224-1322

Insurance

Liability insurance is the responsibility of each individual delegate. Visitors are not covered by the Canadian Medical Health Insurance Plan. Delegates should have their own medical coverage.

Medical Services

Emergency treatment is available at the University Hospital located on campus, tel: 822-7121. There is also a medical centre in the University Village (See also under Insurance and Emergency Telephone Numbers).

Messages

There is a message board located in the IRC Lobby next to the Registration Desk. Please check the board for messages addressed to yourself as well!

Phone messages may be received by the Registration Desk at (604) 822-1156 from 08:00 on Monday, August 3 until 17:00 on Friday, August 7. They will be posted on the message board in the IRC Lobby. When calls cannot be answered in person, a message may be left on the voice mail.

Messages for delegates staying in the Walter Gage Residence may be left by calling the Reservations Office at (604) 822-1010. All suites have voice mail. Single rooms with shared washrooms are not equipped with phones, but messages will be posted on the Gage Message Board in the Lobby.

General Information

Recreation and Sports Facilities

The campus is home to various museums, including the world-renowned Museum of Anthropology, botanical gardens and sports facilities. Brochures and schedules are available at the Registration Desk and at the Walter Gage Residence Front Desk

Golf: The University Golf Course is an 18 hole public course within 15 minutes walking distance of campus; equipment rental is available.

Swimming: The Aquatic Centre is located next to the Student Union Building. Conference delegates may, on presentation of a conference name badge or residence room key, use the facilities at the same time and rates as faculty and staff.

Walking and Hiking: Pacific Spirit Park is a wilderness area surrounding the campus to the south and east. Several well-marked trails facilitate hikes throughout the forest area. Several beaches are also within easy walking distance of the campus.

Outdoor recreation equipment is available for rent on campus.

Registration Desk

The Conference Registration Desk in the IRC Lobby is open from 08:00 each morning, Monday to Friday. Please see our staff for any queries you may have regarding the conference, the campus and Vancouver.

Responsibility

The Organizing Committee assumes no responsibility for accident, losses, damage, delays, or any modifications to the program arising from unforeseeable circumstances. It accepts no responsibility for travel or accommodation arrangements.

The participant acknowledges that he has no right to lodge damage claims against the Organizing Committee should the conference proceedings be hindered or prevented by unexpected political or economic events or generally by acts of god, or should the non-appearance of speakers or other reasons necessitate program changes.

Tour and Information Desk

Located in the lobby of the Walter Gage Residence, our Tour and Information Desk staff will arrange individual sightseeing tours, restaurant reservations and transportation. The phone number is 822-1122.

Transport

Taxis are readily available in front of the Walter Gage Residence. There is also a direct taxi telephone line in the Gage Lobby. To request a taxi pick up from the IRC Building, please see the Registration Desk.

BC Transit buses run from the busloop on campus on a regular basis. Bus schedules are available at the Conference Tourist Information Desk, the Walter Gage Front Desk, and the Student Union Building Main Concourse.

University Village

At the entrance to the UBC campus on University Boulevard (outside Gate 1) is a small shopping centre, within easy (five minutes) walking distance of the Walter Gage Residence and the IRC Building, which includes a bank, pharmacy, photocopying service, computer shop, camera shop, dry cleaner , grocery stores, restaurants and fast food outlets.

Program Overview

TIME	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
8:30	Posters up for Poster Session A	Posters up for Poster Session B		Posters up for Poster Session C	
8:45	S1-N. Weinberg J. Gunn G.A. Arteca	S5-A. Thakkar D.A. Dixon K. Morokuma	S9-J. Cizek K. Dyall G. Schreckenbach	S11-F. Grein G. Billing T. Seideman	S15-T. Ziegler A. Warshel M. Pettitt
10:05	REFRESHMENT BREAK				
10:25	S2-M. Klabowski B. Sanctuary R. Snider B. Shizgal	S6-Vedene H. Smith Jr. M. Gordon M. Thachuk S. Iwata	S10-J. Gunn P. Siegbahn H. Nakatsuji M. Robb	S12-T.W. Dingle M. Head-Gordon G.E. Scuseria A. Becke	S16-R. J. Boyd M. Casida N. Handy
12:25	LUNCH		Harbour Boat Cruise	LUNCH	11:55 am Symposium ends
2:15	S3-W. G. Laidlaw E. Carter J. Tse	S7-B.C. Sanctuary D. Ronis W. Reinhardt		S13-John Cullen P. Bloechl J. Gao	
3:35	REFRESHMENT BREAK			REFRESHMENT BREAK	
3:55	S4-Jim Wright G. Voth M. Klein	S8-D. R. Salahub P. Kusalik J.-L. Rivail		S14-D. Wardlaw M. Kinoshita B. Roux	
5:15	Poster Discussion Session A	Poster Discussion Session B		Poster Discussion Session C	

Program

MONDAY, August 3

8:30 a.m. - 7:15 p.m.	Poster Session A
8:45 a.m. - 10:05 a.m.	Session 1 N. Weinberg (UCFV) Chair J. Gunn (Canada) “Knowledge-based Structure Prediction with the Hierarchical Algorithm” G.A. Arteca (Canada) "Molecular Shape Fluctuations in Polymers and Polymer Networks"
10:05 a.m. - 10:25 a.m	Refreshment Break
10:25 a.m. - 12:25 p.m	Session 2 M. Klabowski (Alberta) Chair: B. Sanctuary (Canada) "Towards Automatic Assignment of 2D and 3D NMR for Proteins" R. Snider (Canada) "Gas Kinetic Theory of Spin Relaxation" B. Shizgal (Canada) "Theory of Planetary Exospheres and Nonthermal Escape"
12:25 p.m.	Lunch
2:15 p.m. - 3:35 p.m.	Session 3 W.G.Laidlaw (Calgary) Chair E. Carter (USA) "Ab Initio Energetics of Extended Systems via Explicit Correlation Embedded in a Density Functional Environment" J. Tse (Canada) "Structrual Principles of Intermetallic Alloys"
3:35 p.m. - 3:55 p.m.	Refreshment Break
3:55 p.m. - 5:15 p.m.	Session 4 Jim Wright (Carlton) Chair G. Voth (USA) "Quantum Dynamical Simulations of Proton Transport in Condensed Phases" M. Klein (USA) "Molecular Dynamics Studies of Ion Channel"
5:15 p.m. - 7:15 p.m.	Poster discussion, Session A

Program

TUESDAY, August 4

8:30 a.m. - 7:15 p.m.	**Poster Session B**
8:45 a.m. - 10:05 a.m.	Session 5 A. Thakkar (UNB) Chair D.A.Dixon (USA) “Applications of Computational Thermochemistry” K. Morokuma (USA) "The Development and Various Applications of the ONIOM method"
10:05 a.m. - 10:25 a.m	Refreshment Break
10:25 a.m. - 12:25 p.m	Session 6 Vedene H. Smith Jr. (Queens) Chair M. Gordon (USA): “Solvent Effects on Chemical Processes” M. Thachuk (Canada) "Dynamics in Intense Laser Fields" S. Iwata (Japan) “Structures of Water Clusters and Metal-Water Cluster Anions, and Photodissociation Dynamics of Ar_n^+
12:25 p.m.	Lunch
2:15 p.m. - 3:35 p.m.	Session 7 B.C. Sanctuary (McGill) Chair D. Ronis (Canada) “Pattern Formation in Non-Equilibrium Systems” W. Reinhardt (USA) "Why is it so Difficult to Simulate Free Energy and Entropy Changes of Molecular Fluids?"
3:35 p.m. - 3:55 p.m.	Refreshment Break
3:55 p.m. - 5:15 p.m.	Session 8 D.R. Salahub (Montreal) Chair P. Kusalik (Canada) "Crystallization of Molecular Liquids: Mechanisms and Techniques" J.-L Rivail (France) "Modelling Structure and Reacivity of Complex Molecular Systems"
5:15 p.m. - 7:15 p.m.	**Poster discussion, Session B**

WEDNESDAY, August 5

8:15 ~~8:45~~ a.m. - 10:05 a.m.	**Session 9** J. Cizek (Waterloo) Chair K. Dyall (USA) "Interfacing Relativistic and Nonrelativistic Methods" G. Schreckenbach (USA) "Density Functional Studies of Relativistic Effects and Magnetic Properties"
10:05 a.m. - 10:25 a.m	Refreshment Break
10:25 a.m. - 12:25 p.m	**Session 10** J.Gunn (Montreal) Chair P. Siegbahn (Sweden) "Quantum Chemical Studies of Metallo Enzymes" H. Nakatsuji (Japan) "SAC-CI Study of the Photosynthetic Reaction Center" M. Robb (UK) "Modelling Photochemistry: Reaction Paths and "on the fly" Semi- classical Dynamics"
12:25 p.m.	**Harbour Boat Cruise**

Program

THURSDAY, August 6

8:30 a.m. - 6:30 p.m.	**Poster Session C**
8:45 a.m. - 10:05 a.m.	**Session 11** F. Grein (UNB) Chair G. Billing (Denmark) "New Semi-Classical Methods for Reactive and Inelastic Molecular Dynamics" T. Seideman (Canada) "Surface Photochemistry: When the Substrate Electrons Get Hot"
10:05 a.m. - 10:25 a.m	Refreshment Break
10:25 a.m. - 12:25 p.m	**Session 12** T.W. Dingle (Victoria) Chair M. Head-Gordon (USA) "New Electronic Structure Methods for Large Molecules and Bond-Breaking" G.E.Scuseria (USA) "A Novel Form for the Exchange-correlation Energy Functional" A. Becke (Canada) "Exploring the Limits of Gradient Corrections in Density-Functional Theory"
12:25 p.m.	Lunch
2:15 p.m. - 3:35 p.m.	**Session 13** John Cullen (Manitoba) Chair P. Bloechl (Switzerland) "Ab-Initio Molecular Dynamics of Methanol and Water in Zeolites" J. Gao (USA) "Combined QM/MM Simulations of Chemical Reactions in Solution and in Enzymes"
3:35 p.m. - 3:55 p.m.	Refreshment Break
3:55 p.m. - 5:15 p.m.	**Session 14** D. Wardlaw (Queens) Chair M. Kinoshita (Japan) "Combination of Monte Carlo Simulated Annealing and RISM Theory for Analyzing Conformational Stability of Peptide in Solvents" B. Roux (Canada) "A Rigorous and Practical Path-Integral Formulation for Computer Simulations for Calculating Rate Constants in Quantum Mechanical Systems"
5:15 p.m. - 6:30 p.m.	**Poster discussion, Session C**
7:00 pm	**Symposium Banquet**

FRIDAY , August 7

8:45 a.m. - 10:05 a.m.	**Session 15** T. Ziegler (Calgary) Chair A. Warshel (USA): Ab Initio Simulations of Chemical Processes in Solutions and Proteins. M. Pettitt (USA) "Phase Stability and Microfolding of Peptides"
10:05 a.m. - 10:25 a.m	Refreshment Break
10:25 a.m. - 11:45 a.m	**Session 16** R.J. Boyd (Dalhousie) Chair M. Casida (Canada) "Molecular Electronic Excitation Spectra From Time-dependent Density-functional Theory: Defining and Extending the Frontiers of TD-DFT" N.Handy (UK) : Density Functionals
11:55 a.m.	**Symposium Ends**

POSTER DISCUSSIONS A, Monday, August 3, 5:15-7:15 p.m.

	Presenter	Title
A1	Aida, M.	Ab initio MD simulations on the hydrolysis of methyl chloride with explicit consideration of 3 water molecules
A2	Alavi, S.	Rate Constants for Recombination Pathways
A3	Altmann, J.A.	An Investigation of the Performance of a New Exchange Correlation Density Functional
A4	Aviyente, V.	Modeling Proton-Bound Clusters of 12-Crown-4-Ether and Dimethoxyethane ("glyme")
A5	Bandyopadhyay, P.	Ab-initio Monte Carlo simulation using multicanonical algorithm: Importance of finite temperature effects on structure and spectroscopy of clusters
A6	Baranowski, R.	Molecular dynamics simulation of gaseous polyatomic ions in electrostatic fields
A7	Block, D.A.	A Statistical Mechanical Examination of the Solvation of Acetic Acid and of Gycine Zwitterion and Neutral Species
A8	Calugareanu, I.	On the Application of Integral Equation Theories to Model Chiral Systems
A9	Cammi, R.	Solvent effects on linear and nonlinear electric properties of Donor-Acceptor polyenes: investigation of electronic and vibrational components in terms of structure and charge distribution changes
A10	Camp, P.J.	Biaxiality in Liquid Crystals
A11	Cann, N.M.	An investigation of surface-induced selectivity
A12	Carmichael, I.	The Performance of Density Functional Theory in Some Difficult Cases
A13	Cavigliasso, G.	Density Functional Calculations of Core-Electron Binding Energies of Boron-Containing Molecules
A14	Chabalowski, C.F.	Preliminary Results for the Interaction of Carbon Monoxide with Iron Surfaces using Planewave Methods

A15	Chen, H.	The Quadrature Discretization Method (QDM) in the solution of the Fokker-Planck and Schroedinger equations
A16	Çinar, Z.	A Computational Study of the Photodecomposition Reactions of Trifluroethylene
A17	Cullen, J.	Semiempirical Methods which Go Beyond the Minimal Basis Set
A18	Cullen, J.	An Examination of the GVB Approach Using an INDO Model Hamiltonian
A19	Das, B.	Separation of Chiral Particles in an Enantiomeric Mixture
A20	Day, T.J.F.	The Dynamics of Selective Solvation in Binary Solvents: An MD Study
A21	Dehareng, D.	Proposition for the acylation mechanism of serine proteases
A22	Doerksen, R.J.	Electron-correlated polarizabilities of 87 five- and six-membered-ring azaboracycles
A23	Dokalik, A.	NMR-Shieldings and Vibrational Spectra of small N-Heterocycles: Experimental versus ab initio calculated data
A24	East, A.L.L.	The Sixteen Valence Electronic States of Nitric Oxide Dimer $(N0)_2$
A25	Eliav, E.	The Multireference Relativistic Coupled Cluster Method: Some recent developments
A26	Field, M.J.	Hybrid Quantum Mechanical and Molecular Mechanical Potentials for Studying Reactions in Proteins and in Solution
A27	Gauld, J.W.	Oxidative degradation of radical-containing enzymes
A28	Goddard, J.D.	The Biradical Characters of 1,2-Dithiin, 1,2-Dioxin and Their Valence Isomers
A29	Goryachev, A.	Synchronization Defects and Transition to Turbulence in Spiral Waves
A30	Grein, F.	Electronic g-tensors of molecules: Significance of electron correlation
A31	Gunn, J.R.	Knowledge-based Structure Prediction with the Hierarchical Algorithm

A32	Gurin, V.S.	*Ab initio* Calculation of the Electronic Structure of Cadmium Sulfide Cluster Fragments Prepared with Stabilizing Thiolate Ligands
A33	Gutowski, M.	Density Function Theory Study of Water Adsorption on the MgO (001) Surface
A34	Hatipoğlu, A.	Structure-Activity Relations for the Gas-Phase Reactions of Hydroxyl Radicals with Aliphatic Alcohols
A35	Head, J.D.	A Quantum Chemical Investigation of Hydrated Halide Adsorption on the Cathodic Al(111) Surface
A36	Hirata, S.	Development and application of analytical energy gradient methods in correlated crystal orbital theories
A37	Ishida, T.	Penning ionization from attractive superexcited states: H_20 + He* → H_20^+ + He + e^-
A38	Ishikawa, Y.	*Ab initio* molecular dynamics simulations of the interaction of $N0_2^+$ with clusters of three and four water molecules
A39	Jack, D.B.	Structure and Phase Transitions of CO Adsorbed in Insulator Surfaces (NaCl, LiF, MgO)
A40	Jayatilaka, D.	Extracting the Current Density from Experiment
A41	Jonsson, D.	Ab initio calculations for the Cotton-Mouton effect for CO_2, N_2O, OCS and CS_2
A42	Kay, K.G.	Uniform Semiclassical Treatments for Time-Independent and Time-Dependent Wave Functions
A43	Kochanski, E.	Theoretical Study of the $OH^-(H_2O)_n$ System
A44	Komatsuzaki, T.	Chaotic and Regular Dynamics of Isomerization Reaction of Ar_6 Cluster: Origin of Collective Motions & Dividing Surface free from Recrossing Problem
A45	Krauss, M.	Structure and spectroscopy of the cobalt substituted lactamase from *bacteroides fragilis*
A46	Leszczynski, J.	Computational Design of Clay Minerals: Hydration of Na^+ Exchange Cation Placed on the Basal Surface of Clay Minerals
A47	Liu, Z.F.	Ab Initio Molecular Dynamics Study on Ag_n, with n=4,5,6

A48	Lohr, L.L.	Paramagnetically Induced NMR Relaxation in Solutions Containing $S \geq 1$ Ions: A New Theoretical Model
A49	Lushington, G.H.	Ab Initio Simulation of Physisorption: N_2 on Graphite
A50	Maclagan, R.G.A.R.	Quantum Chemical Calculations on Ion-Molecule Processes
A51	Martell, J.M.	Transition States for 1,2 Elimination of HX (X = F, Cl) from Trifluoroethane and Chloroethane: Test Case Studies
A52	Martins, J.B.L.	Cluster model study of ZnO relaxation
A53	Martins, J.B.L.	A PM3 Theoretical Study of Coverage Effects for water dissociation on the MgO (001) Surfaces
A54	Matsuzawa, H.	Theoretical Study on Fluoranthene-2,3-Dichloro-5, 6-Dicyano-*p*-Benzoquinone (DDQ)
A55	McCourt, F.R.W.	*Ab inito*-based potential energy surfaces and related properties of the ground state $RgCl_2$ complexes: the linear conformer effects
A56	McWhirter, J.L.	Nonequilibrium Molecular Dynamics Simulations of Simple Dipolar Fluids
A57	Mebel, A.M.	Ab Initio Studies of Photochemistry of Ethylene: Vibronic Spectra, Rates of Internal Conversion, and Photodissociation Rate Constants
A58	Meijer, A.J.H.M.	Time-dependent quantum mechanical calculations on $H + O_2$ for total angular momentum $J > 0$
A59	Mennuci, B.	The Linear Response Theory for the Polarizable Continuum Model
A60	Mola, E.	Preferential Adsorption Sits for H_2CO and H_2O over V_2O_5

POSTER DISCUSSIONS B, Tuesday, August 4, 5:15-7:15 p.m.

	Presenter	**Title**
B1	Muchall, H.M.	Computational studies on π_N and Σ_N states of azolidinone and oxazolidinone radicals
B2	Napier, D.	Gas Kinetic Theory of Sound Dispersion in Two-Component Systems

B3	Nguyen, N.-A.	Symbolic Calculations of Unitary Transformations in Quantum Dynamics
B4	Nicklass, A.	The Interplay of Spin-Orbit Coupling and Electron Correlation in Atoms and Small Molecules
B5	Nielsen, S.	Colouring a Lorentz Gas
B6	Ortiz, J.V.	Electron Propagators for Large Molecules and for Highly Correlated Reference States
B7	Ötke, A.N.	Hardness Profile of Conjugated Polymers
B8	Otto, F.	Pressure Between Two Walls Immersed in Electrolyte Solution: Solvent Induced Effects
B9	Ouamerali, O.	Stability of doubly $H_2P_2O_7^{2-}$ and triply $HP_2O_7^{3-}$ charged anion in gas phase
B10	Paci, J.	Strong Field Dissociation of HCl^+ – A Comparison of Kinetic Energy Distributions
B11	Pappalardo, G.C.	Molecular Dynamics (MD) Simulations and Energy Dispersive X-Ray Diffraction (EDXD) Studies of the Structure of Semicrystalline Poly[bis(phenoyx)phosphazene]
B12	Patchkovskii, S.	NMR chemical shifts in MNDO approximation: Parameters and results for H, C, N, and O.
B13	Peraza, J.A.	Theoretical Study of the Interaction of Small Clusters of IrPt with H_2.
B14	Percus, J.K.	Gauge Field Optimization of Classical Fluid Expansions
B15	Petitjean, L.	Comparison between ethylene and propylene polymerization mechanisms with zirconocene catalysts
B16	Pires, J.M.	Semiempirical energy calculations on the myelin basic epitope protein MPB_{74-85}: elaboration of agonist and antagonist motifs in autoimmune disease
B17	Pitchko, V.	Prediction of the Rates of Hydration of Simple Carbonyl Compounds Using the ECDE Method
B18	Polly, R.	Absorption spectrum of chromone: A study applying and comparing the CASSCF/CASPT2 and the time-dependent density functional method

B19	Polson, J.M.	Simulation of solid-fluid phase equilibria for systems of chain molecules
B20	Pye, C.C.	An Implementation of the COSMO Solvation Model in the Density Functional Package ADF. Part II. Refinement, Testing, and Applications
B21	Rabaâ, H.	Electronic and Structural Effects of Nitrogen Doping on the Ionic Conductivity of γ-Li_3PO_4
B22	Raynor, S.	The Theoretical Treatment of Infinitely Periodic Hydrogen-Bonded Systems
B23	Roy, P.-N.	Extension of the Centroid Molecular Dynamics formalism to include quantum statistics
B24	Sağ Erdem, S.	A computational study of the reactivity of diethenylnaphthalenes towards anionic polymerization
B25	Sakai, Shogo	Theoretical Studies on the Cyclic Reaction Mechanisms for s-cis Butadiene: Ground and Excited States
B26	Salahub, D.R.	Performance of Density Functionals for Transition States
B27	Schäfer, L.	Ab initio geometry determinations of proteins
B28	Schäfer, L.	Molecular Dynamics Simulations of the Sorption of Organic Compounds at the Clay Mineral/Aqueous Solution Interface
B29	Schmid, R.	Polymerization Catalysts with d^n-Electronics (n=1-4): A Theoretical Investigation on Model Systems
B30	Schmider, H.L.	Density Functionals From the Extended G2 Test Set
B31	Schreckenbach, G.	Uranyl Tetrahydroxide (VI), $[UO_2(OH)4]^{2-}$ – A Theoretical Study
B32	Seidl, M.	Strictly Correlated Electrons and the Correlation Energy of Real Systems
B33	Selçuki, C.	A DFT Study of Substitutent Effects on the Conversion of Carbonyl Oxides to Dioxiranes
B34	Shim, I.	All Electron *ab initio* Investigations of the Electronic States of the Iron Group Carbides, FeC, CoC, and NiC
B35	Shizgal, B.D.	Doppler Profiles of the Distribution of $O(^1D)$ Relaxing in Ne

B36	Siebrand, W.	Proton Tunneling in Polyatomic Molecules: A Direct-Dynamics Instanton Approach
B37	Simperler, A.	Hydrogen Bonding in 2,6-Disubstituted Phenols: Competitive Hydrogen Bonds and Hydrogen Bond Equilibria
B38	Srinivas, G.N.	Theoretical Studies on Boron-Lithium Clusters
B39	Su, M.-D.	A Theoretical Model for the Orientation of 16-Electron CpML Insertion into the C-H Bond of Propane and Cylopropane and Its Regio- and Stereoselectivity
B40	Sundholm, D.	Density Functional Theory Calculations of Excitation Energies of Porphyrins
B41	Takano, Keiko	An *ab Initio* MO Study on the Isomers of Phosphenium Complexes of Group 6 Transition Metals
B42	Tao, F.-M.	The Effect of Water on the Tautomerization of Guanine
B43	Tokiwa, H.	Conformational Analysis of Oligopeptides
B44	Tokiwa, H.	Is InOH a quasi-linear molecule?
B45	Torrens, F.	Fractal hybrid orbitals in iron proteins
B46	Turner, R.E.	Quantum Boltzmann Equations and Muonium Interactions with Gases
B47	Uehara, K.	First-principles LAPW-MD calculations on small transition metal clusters
B48	Vanquickenborne, L.G.	Electronic Structure of Transition Metal Complexes with Low-Coordinated Phosphorus Ligands
B49	Varnali, T.	Unimolecular [2+2+2] Cycloaddition reaction for [3.3.3] Undeca-2,7,9-Triene
B50	Wang, R.L.C.	Contribution of Unoccupied Cu sp States to Chemical Vibrational Frequency Shifts of CO on Cu(111)
B51	Waroqier, M.	Many-body perturbation techniques in the Kohn-Sham Density-Functional-Theory
B52	Wetmore, S.D.	The Effects of Radiation on DNA Studied by Density Functional Theory

B53	Whitehead, M.A.	Tin Alkynyl Bonding to Surfaces: Co-polymerisation and Quantum Calculations
B54	Wilkie, J.	A Jastrow Corrected Time-Dependent Self-Consistent Field Approximation
B55	Wolf, K.	A comparative PAW *ab initio* molecular dynamics study of proton transfer in 5,8-dihydroxynaphthoquinone and the formic acid dimer
B56	Wolff, S.K.	Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling
B57	Wright, J.S.	Accurate Thermochemistry for Large Molecules using a Density Functional/Locally Dense Basis Set Approach

POSTER DISCUSSIONS C, Thursday, August 6, 5:15-6:30 p.m.

	Presenter	Title
C1	Murashov, V.V.	Thermal Conductivity of Model Zeolites: Molecular Dynamics Simulation Study

ABSTRACTS

Ab initio MD simulations on the hydrolysis of methyl chloride with explicit consideration of 3 water molecules

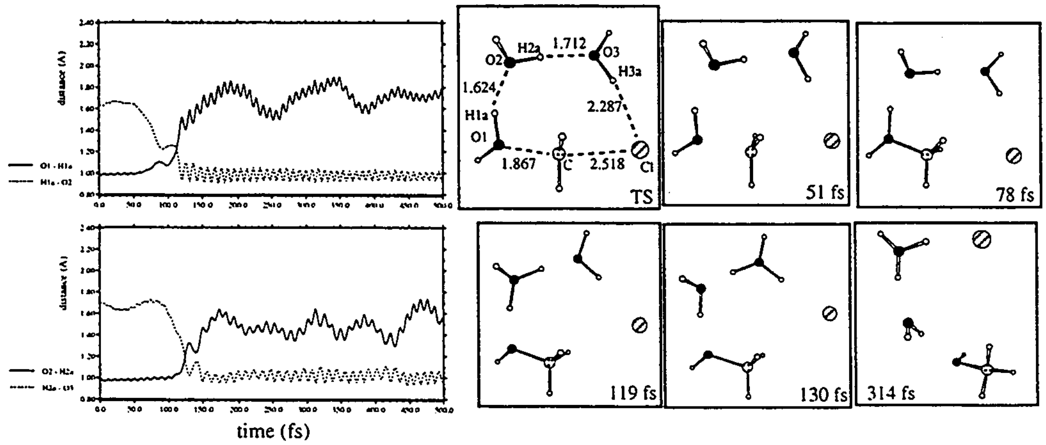
Misako Aida, Hiroshi Yamataka and Michel Dupuis

Biophysics Division, National Cancer Center Research Institute,
5-1-1 Tsukiji, Chuo-ku,Tokyo, 104-0045 Japan

INTRODUCTION: Solvent plays an important role in determining rates of reactions in solution and in defining reaction characteristics. S_N2 reactions in solution are among the most extensively studied chemical reactions. Understanding of the role of the solvent at the molecular level, however, is still incomplete, as experimental techniques that probe solute/solvent interactions at the level of individual molecules are not available. Here we apply the ab initio molecular dynamics (MD) simulation method with quantum energies and forces to the hydrolysis reaction of methyl chloride with explicit consideration of 'solvent' molecules. We aim at obtaining a molecular level understanding of the dynamics of S_N2 reactions in solution and of the active role of the solvent molecules in these reactions.

METHOD: Ab Initio MD simulations of the hydrolysis reaction of methyl chloride were performed with explicit consideration of two 'solvent' water molecules in addition to the 'solute' water molecule. This system was selected as the smallest prototypical system that displays characteristic features found in quantum chemical studies involving larger 'solvent' clusters. Trajectories were initiated in the transition state region. Energies and forces were obtained at the HF/6-31G level. The classical nuclear trajectories were obtained using a fourth-order Gear predictor-corrector algorithm. A time step of 0.5 fs was used for the present simulations. The temperature of the system is associated with the classical kinetic energy, and it was scaled to be approximately constant (298 K) during the trajectories. The program package of HONDO96 was used for the ab initio MD calculations.

RESULTS: We performed 9 simulations at 298 K with different initial velocities, all of them starting from TS. In some of the simulation runs, the system was found to evolve in the backward direction, i.e. to move toward the initial state; in other runs, the trajectory proceeded in the forward direction toward the product state. One of the simulations corresponding to the forward reaction is shown below, with some snapshot structures along the trajectory. The simulations clearly showed the existence of and the dynamical characteristics of two nearly concerted proton transfers involving the attacking water molecule and the solvent water molecules on the way to formation of the products. The observation of these proton transfers points clearly to the need for an explicit quantum chemical treatment of at least a few solvent water molecules to describe the methyl chloride solvolysis.



Rate Constants for Recombination Pathways

G. W. Wei, **Saman Alavi**, and R. F. Snider
Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1

Recombination reactions involve the formation of a chemical bond between two free species. Four elementary mechanisms can be written for a recombination reaction. The *direct* mechanism, involves an almost instantaneous, termolecular entry of the three molecules into the interaction region,

$$A + B + C \xrightarrow{0} AB + C. \tag{1}$$

The three *indirect* mechanisms involve the bimolecular formation of a reaction intermediate or transient colliding pair with positive relative energy, which then collides with a third molecule. The excess kinetic energy is carried away by species C after the second bimolecular collision, and the negative energy bound state AB is formed. Indirect mechanisms are further classified as being *energy transfer*,

$$A + B + C \xrightarrow{1} A\cdots B + C \xrightarrow{1'} AB + C, \tag{2}$$

or *exchange* mechanisms,

$$A + B + C \xrightarrow{2} A\cdots C + B \xrightarrow{2'} AB + C, \tag{3}$$

$$A + B + C \xrightarrow{3} B\cdots C + A \xrightarrow{3'} AB + C, \tag{4}$$

the name of the mechanisms reflecting the nature of the process which occurs in the final step in order to produce AB.

By using the formal theory of three-body collision dynamics, it is be illustrated that contrary to usual chemical intuition, the rate constants, calculated exactly for all four pathways are *rigorously equal* and each pathway separately describes the complete dynamics of the recombination. The central part of the proof involves showing that the Møller superoperator for the direct pathway is equivalent to the ordered product of the two Møller superoperators which represent the two steps of any of the indirect pathways. For example, for the Møller superoperators involved in the direct and energy transfer mechanisms it is shown that,

$$\Omega_{(AB,C\leftarrow A,B,C)} = \Omega_{(AB,C\leftarrow A\cdots B,C)}\ \Omega_{(A\cdots B,C\leftarrow A,B,C)} \tag{5}$$

Møller superoperators are related to the transition superoperators for elementary reactions. These in turn are involved in expressions for the transition probabilities from reactants to products for each reaction. By using the above stated relations between the Møller superoperators, equality of the rate constants for the four mechanisms can be demonstrated.
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An Investigation of the Performance of a New Exchange-Correlation Density Functional

Julianna A. Altmann and Nicholas C. Handy[a]

Department of Chemistry, King's College London, Strand, London
WC2R 2LS, UK

This investigation is part of our continuing study of molecular properties of sulfur-containing molecules using Density Functional Theory.

Previously, we found that DFT methods tend to overestimate the bond distances of these compounds to various extent; the most serious errors occurrred in cases where sulfur was bonded to halogens[1]. We also found that, by using the hybrid functional B3P86 and large basis sets, such errors could be reduced considerably to a level comparable to MP2 results[2]. Moreover, the harmonic frequencies predicted by B3P86 were closer to experiments than the predictions arising from both Hartree Fock and MP2 methodologies[2].

We now extended our investigations to assess the latest member of a new class of GGA density functionals, called HCTH, developed recently by Handy and coworkers[3]. We report structural parameters computed for our previous benchmark of 20 sulfur-containing molecules, using gaussian basis sets of triple zeta plus polarization functions quality. These are compared with predictions arising from Hartree Fock, MP2, B3P86 and BLYP methodologies as well as with experiment. Preliminary results indicate that HCTH predicts geometries that are a considerable improvement over BLYP and are comparable to B3P86.

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[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Molecular shape fluctuations in polymers and polymer networks

Gustavo A. Arteca

Département de Chimie et Biochimie, Laurentian University,
Ramsey Lake Road, Sudbury (Ontario), Canada P3E 2C6.

When monitoring molecular motions, polymer chains can behave as if they were effectively *entangled* with their neighbours or with themselves (even when they do *not* form knots or links). These entanglements are the essential feature behind the physics of polymer solutions and melts. Similarly, the characterization of self-entanglements in a single chain sheds light on its structure and stability. For most chains, one must rely on *geometrical* (rather than topological) measures of entanglement complexity. In this communication, I will discuss the recent progress on the theory and applications of these geometrical shape descriptors. Particular attention is devoted to the measures based on the *overcrossing probabilities* (and the mean overcrossing number, $\overline{N}$) of space curves.(1) This descriptor provides a physically intuitive characterization of self-entanglements in a chain or entanglements in a network. Recent work has begun to uncover some properties of $\overline{N}$ in single chains, *e.g.*, configurationally-averaged model chains and (experimental) protein native states exhibit power-law scaling with the number of monomers.(2) From the dynamic viewpoint, fluctuations in $\overline{N}$ are found to accompany some configurational transitions.(3) These changes in $\overline{N}$ provide important information on molecular shape not readily available from other descriptors (*e.g.*, molecular size). Here, I will review these results and discuss how an efficient analysis of entanglement complexity can be used to gain an understanding on the behaviour of entangled polymers and solvation networks.

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Modeling Proton-Bound Clusters of 12-Crown-4-Ether and Dimethoxyethane ("glyme")

Dora Adötoledo*, **Viktorya Aviyente***, Jan M. L. Martin** and Chava Lifshitz#,¶

* Chemistry Department, Boğaziçi University, 80815, Bebek, Istanbul, Turkey.

The association reactions undergone by $Cr4.H^+$ with NH_3, CH_3OH, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ have been studied using the B3LYP density functional method and a variety of basis sets. For comparison purposes the insertion reactions for the same bases into $Gl.H^+$ and $(Gl)_2H^+$ have also been modeled. The B3LYP/aug-cc-pVDZ//B3LYP/4-21G(*) level of theory was found to be a particularly favorable compromise between accuracy and computational expense for the calculation of proton affinities of medium-sized species. Reference geometries and harmonic frequencies (whence zero-point energies and thermal corrections at 298 K) were obtained at the B3LYP/4-21G(*) level. The two most favorable, and essentially isoenergetic, conformers of dimethoxyethane (glyme) have been found to be *ttt* and *tgt*, in agreement with high-level ab initio studies, while a protonated *tgt* conformer with the proton included in a central five-membered ring is the most stable conformer for $Gl.H^+$. The protonated glyme, $Gl.H^+$, the protonated diglyme, $(Gl)_2H^+$ and the protonated crown ether, $Cr4.H^+$ form two internal hydrogen bonds with NH_3, CH_3OH, CH_3NH_2 and $(CH_3)_2NH$; except for $(Gl)_2H^+.NH_3$ which has four O...H bonds, and for $Gl.NH(CH_3)_3^+$, in which there is a single O..H bond and the protons of the methyl groups assist weakly in O...HC bonding. The association energy between the protonated central base and the ligands decreases, while the insertion energy increases, with increasing proton affinity of the inserting base (NH_3 or CH_3OH). Trimethylamine does not follow the expected trend because it forms proton bound clusters which have a single O...HN bond instead of two.

** Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel.
# Department of Physical Chemistry and the Farkas Center for Light Induced Processes,
The Hebrew University of Jerusalem, 91904, Jerusalem, Israel.
¶ Archie and Marjorie Sherman Professor of Chemistry

Ab-initio Monte Carlo simulation using multicanonical algorithm: Importance of finite temperature effects on structure and spectroscopy of clusters.

Pradipta Bandyopadhyay, Seiichiro Ten-no and Suehiro Iwata

Graduate University for advanced studies and Institute for Molecular Science,
Okazaki- 444-8585, JAPAN

Theoretical studies of finite temperature effects on molecular spectra and properties are rare but extremely important. Ab-initio simulation techniques, though promising, suffer from the enormous computational cost to study the finite temperature effects. Multicanonical algorithm/reweighting technique is an efficient tool to study finite temperature effects [1,2]. In this algorithm the system can explore any part of the potential energy surface with equal ease and get the reweighted canonical distribution for any temperature from only a single run making finite temperature studies computationally tractable. In this series of works the algorithm are combined with the ab initio MO calculations.

As a test example it was first applied to water dimer [3]. The potential energies have been calculated at the RHF / 6-31G* level of theory. Analysis of the radial and angular distribution functions show how with the increase of temperature thermally accessible states contribute to the average structure. With the increase of temperature structures, similar to the C_i transition state contributes considerably to the average structure.

It has been suggested that the complex photoelectron spectra of silicon-carbon anion clusters [4] is due to the presence of several isomers at the experimental conditions. Doublet $Si_2C_2^-$ and $Si_3C_3^-$ have been calculated by ROHF method. The energy difference between the anion and neutral is approximated by Koopman's theorem neglecting orbital relaxation. Preliminary results of the simulation show that indeed presence of several isomers can lead to these complex spectra.

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Molecular dynamics simulation of gaseous polyatomic ions in electrostatic fields

Roman Baranowski Mark Thachuk

Chemistry Department, University of British Columbia
2036 Main Mall, Vancouver, Canada
V6T 1Z1

A molecular dynamics simulation of the motion of polyatomic ions in neutral gases under the influence of homogeneous electrostatic fields is presented. In particular, we calculate ion transport coefficients and investigate dependencies of these properties on different geometries of the ion, interaction potentials, charge distributions and field strengths. The resulting ion mobilities are compared with the available experimental data and can be used to obtain structural information for polyatomic ions in the gaseous phase.

New semiclassical methods for inelastic and reactive molecular dynamics

Gert D. Billing
Department of Chemistry, H. C. Ørsted Institute
University of Copenhagen, 2100 Copenhagen Ø
Denmark

Due to the many channel nature of the full quantum dynamical treatment of the dynamics of molecular reaction processes, the solution of the problem is even for triatomic systems non-trivial if the atoms are either heavy or if more than one potential energy surface is involved. The situation becomes og course even worse for larger systems. Obviously alternative methods which involve some approximations have to be developed.

We have recently formulated a method based on a semi-classical approach to the dynamics. This approach treats approximately some degrees of freedom, i.e. "classically" whereas others are quantized.

The classical limit is obtained in a systematic and selfconsistent fashion by introducing a quantum basis set which in the limit contains classical mechanics in the form of trajectories governing the motion of a Gaussian wave packet. In this manner the socalled primitive quantum-classical theory is obtained. In this approach the two subsystems are simply coupled by a mean field potential. The method does however provide systematic ways, in which it can be improved. That is correction terms to the Gaussian wave packet can be introduced. In this manner the time-dependent selfconsistent field method is obtained. However, it is important that we can improve both the primitive and the corrected classical path theories by introducing a variational determination of the initial momentum P_0 and width of the wavepacket α_0. Hereby the corrected Ehrenfest approach is obtained [1]. This approach is closely connected to the symmetrized Ehrenfest approach suggested many years ago [2].

Another important feature is that the approach provides us with a way of measuring the coupling or correlation between the "classical" and quantum subsystems. This is done by introducing corrections in the time-dependent multiconfiguration selfconsistent field direction. Either by the multi-trajectory or the Hermite correction methods [3]. This is important since the quantum-classical approach in its limit assumes a weak coupling between the two systems. Hence it is important to look for coordinates which are separable (in a dynamical sense) before the approximation is invoked.

More recently the approach has been used to formulate a "classical" molecular dynamics which is capable of fealing quantum friction, i.e. the dynamics moves close to the classical limit but picks up quantum features when present.

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Ab-Initio Molecular Dynamics of Methanol and Water in Zeolites

P.E. Blöchl

IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

E. Nusterer and K. Schwarz

Vienna University of Technology, A-1060 Vienna, Austria

Adsorption of methanol and other small molecules in zeolites has been studied extensively in the past decade. However, their adsorption structure is still subject to debate. Our work focuses on the adsorption structure of methanol and water as they interact with acid sites in low-alumina sodalite. These simple molecules are important for many technical processes, such as the methanol-to-gasoline process. To investigate the structure and dynamics at finite temperatures, we have used the *ab-initio* molecular dynamics approach in combination with the Projector Augmented Wave method. We show that at low coverages no protonation takes place, which is confirmed by comparing the vibrational properties with measured i.r. spectra. Spontaneous protonation takes place at higher coverages, which is consistent with the catalytic activity of zeolites for acid-catalized reactions.

A Statistical Mechanical Examination of the Solvation of Acetic Acid and of Glycine Zwitterion and Neutral Species

D. A. Block, A. Rauk, D. A. Armstrong

Department of Chemistry,
University of Calgary,
Calgary, AB, Canada T2N 1N4

A good test of any solvation method is whether it can reproduce the experimentally observed preference for the zwitterionic form of glycine over the neutral form in solution. In high level ab initio gas phase studies, the neutral form is the only stable structure. A Monte Carlo solvation study of the glycine system was undertaken in order to determine both relative and absolute free energies of solvation. The structures used were solution structures as determined by Gaussian 94's Self Consistent Isodensity Polarized Continuum Model, using the B3LYP hybrid functional and the 6-31G(D) basis set. The electronic energies of these structures were combined with the free energies of solvation found by BOSS 3.8, a Monte Carlo statistical mechanics package. This combination reproduces what experimental evidence there is satisfactorily, and gives reasonable values for other quantities not available to experiment.

In order to discover absolute free energies of solvation, it was necessary to perturb the glycine system through acetic acid and methane to nothing. As a tangential study, some conformational issues relating to acetic acid are being re-examined. All the values discovered here are compared with available experimental and previous computational data. Glycine zwitterion is found to be preferentially solvated by about 129 kJ/mol over the neutral form. This combined with the difference in electronic energy gives a total preference for the zwitterion of 31 kJ/mol.

On the Application of Integral Equation Theories to Model Chiral Systems

Irina Calugareanu, Natalie Cann

Department of Chemistry, Queen's University, Kingston, K7L 3N6 Canada

Chirality can confer dramatically different biological properties to enantiomeric molecules. Because enantiomers have similar physical properties, they are very difficult to separate and quantitate efficiently. Yet, the major importance of chiral particles is due to the behavior of individual enantiomers. We are interested in the study of structure and properties of systems involving simple chiral particles. The development and application of integral equation based approaches (in particular HNC, RISM) to structure determination in these systems will be discussed. Emphasis will be placed on the advantages, disadvantages and challenges involved with each approach.

Solvent effects on linear and nonlinear electric properties of Donor-Acceptor polyenes: investigation of electronic and vibrational components in terms of structure and charge distribution changes.

Roberto Cammi[1], Benedetta Mennucci[2] and Jacopo Tomasi[2]*
[1]Dipartimento di Chimica Generale ed Inorganica.
Università di Parma, viale delle Scienze, 43100 Parma, Italy
[2]Dipartimento di Chimica e Chimica Industriale.
Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy

March 5, 1998

Abstract

We investigate the influence of solvation media upon the relationship between the structure, spatial distribution of electron density, and linear and nonlinear electric properties for two series of push-pull π-conjugated molecules. The analysis is performed on both electronic and vibrational components of static polarizability and first hyperpolarizability, and the effects solvent induce on them are analyzed singularly within the framework of the polarization continuum model. Solvent is found to affect the extent of charge separation induced in the ground state of these molecules. This charge separation leads to a geometric distortion, measured by the bond-length-alternation (BLA) parameter, which shows a solvent-induced evolution of the molecular geometry from a neutral, bond-alternated polyene-like structure, to a partially ionic cyanine-like structure, and ultimately to a ionic bond-alternated structure. As a consequence large changes in the linear and nonlinear response properties are found, both in their electronic and vibrational contributions. Regarding the latter, we recall that studies on vibrational (hyper)polarizabilities for molecular systems in solution are presented here for the first time.

BIAXIALITY IN LIQUID CRYSTALS

Philip J. Camp [1] and Michael P. Allen

H. H. Wills Physics Laboratory, University of Bristol
Royal Fort, Tyndall Avenue, Bristol BS8 1TL, UK

In a uniaxial nematic liquid crystal the molecules are orientationally aligned along the bulk director. Using computer simulations, we investigate three different fluids of non-spherical particles in which there are *two* such directors.

(1) A fluid of biaxial hard ellipsoids, with semi-axes $a \neq b \neq c$, where each semi-axis has its own direction of alignment. This is an example of a biaxial nematic phase. It is found to occur for only a narrow range of particle geometries.

(2) A fluid mixture of ellipsoidal rods and plates, where each component has its own (orthogonal) direction of alignment. Interestingly, at high densities the mixture tends to demix into two uniaxial phases, one rich in rods, the other rich in plates.

(3) A fluid of banana-shaped molecules with transverse "dipoles" acted upon by an external field. In the absence of an external field the fluid can exhibit a uniaxial nematic phase. When the dipoles are forced to align, a bend in the long-axis director field is generated; this is the *flexoelectric effect.*

In each case we highlight the connection between our simulation results and experimental observation.

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[1] Present address: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, Canada V6T 1Z1.

An investigation of surface-induced selectivity

N.M. Cann

Department of Chemistry, Queen's University, Kingston, Canada, K7L 3N6

The ability of a surface to distinguish between a mixture of similar particles has been investigated using integral-equation theories. Various mixtures will be discussed and results are presented for mixtures of particles differing only in size. For these mixtures, the relationship between the degree of size similarity, the nature of the interactions with the surface, and surface selectivity is investigated in detail. The role of the solvent (SPCE water) on this relationship has been considered for hydrophobic surfaces.

The integral-equation theories employed in this work will be discussed with emphasis placed on improvements in accuracy important in the investigation of mixtures of similar particles. In particular, bridge diagrams are presented for several of the systems considered.

The Performance of Density Functional Theory in Some Difficult Cases

Ian Carmichael

Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556
USA

Density Functional Theory (DFT) has become a ubiquitous tool in computational quantum chemistry. Since DFT methods have been incorporated into a number of popular *ab initio* molecular-orbital program packages they can be (and are being) used as a "black-box" to provide answers in a wide variety of situations.

Some of the drawbacks of such an approach to the routine investigation of important chemical problems are pointed out here. Limiting values from DFT calculations are compared to experiment and to the results from high-level coupled-cluster treatments in some computationally difficult systems.

We examine magnetic hyperfine coupling and electron loss and attachment energetics in atoms, indirect nuclear spin-spin coupling in diatomics, and structural rearrangements, including dissociation, in symmetrical π^*- and σ^*-radical cations.

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MOLECULAR ELECTRONIC EXCITATION SPECTRA FROM TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY: DEFINING AND EXTENDING THE FRONTIERS OF TD-DFT

Mark E. Casida

Département de chimie, L'Université de Montréal
C.P. 6128, Succursale centre-ville
Montréal, Québec H3C 3J7, Canada
Mark.Casida@umontreal.ca

Density-functional theory (DFT) has proven to be a remarkably simple yet effective method for first-principles calculation of a variety of molecular properties. However important problems in the study of optical materials, spectroscopy, and photochemistry require an extension of the traditional Hohenberg–Kohn–Sham formalism, which is restricted to ground state time-independent properties. Time-dependent DFT (TD-DFT) provides a suitable formal extension. A few years ago, we developed a molecular formulation of TD-DFT for use in a quantum chemical context. While this approach can be applied to the calculation of a variety of molecular response properties, the present talk will focus on electronic excitation energies. In view of the large number and variety of electronic excitations (even within a single molecule), this provides a severe testing ground for exchange-correlation functionals. TD-DFT gives remarkably good results for low-lying excitations, when the local density approximation is used. However, use of a functional yielding an exchange-correlation potential with the correct asymptotic behavior is critical for high-lying excitations. In this talk, I will elaborate on our present understanding of the strengths and limitations of TD-DFT for practical calculations of excitation spectra.

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AB INITIO ENERGETICS OF EXTENDED SYSTEMS VIA EXPLICIT CORRELATION EMBEDDED IN A DENSITY FUNCTIONAL ENVIRONMENT

Niranjan Govind, Yan A. Wang, and **Emily A. Carter**

Department of Chemistry and Biochemistry
Box 951569, UCLA, Los Angeles, CA 90095-1569 U.S.A.

Abstract

We present a new embedding technique that combines density functional theory (DFT) and explicit electron-correlation methods. We construct a periodic-DFT-based embedding potential as a local one-electron operator within more accurate electron-correlation calculations. We demonstrate how DFT calculations can be systematically improved via this procedure. The method involves an orbital-free kinetic energy density functional in the embedding operator. This allows one to express the embedding operator strictly in terms of the total density of the system and the density in the region of interest. In this way, we obviate the need to form a set of localized orbitals to describe the electrons in the surrounding environment. This is especially important in the systems in which we are most interested, periodic metallic surfaces, where the absence of a band gap renders exponential localization impossible. This way of expressing the embedding operator also eliminates any problems with matching conditions at the embedding boundary, or spurious charge transfer, since the electrostatic potential and the density is continuous by construction. We benchmarked the method against nearly exact calculations on a small system and then further corroborated it on an experimentally well-studied chemisorption system, CO on Cu(111). Our binding energies are in good agreement with nearly full configuration interactions in the former and experimental adsorbate binding energies in the latter. If time permits, we will discuss other improvements to the theory and other applications as well.

DENSITY FUNCTIONAL CALCULATION OF CORE-ELECTRON BINDING ENERGIES OF BORON-CONTAINING MOLECULES

Germán Cavigliasso, Ching-Hang Hu, Delano P. Chong

Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, V6T 1Z1 Canada

In recent studies of Density Functional Theory (DFT) [1, 2], we found a method of calculating accurate core-electron binding energies (CEBEs). Our approach involves the use of the unrestricted generalized transition state model, a exchange-correlation potential based on a combined functional of Becke's exchange (B88) and Perdew's correlation (P86), and a scaled polarized valence triple-zeta (s-pvtz) basis set.

Our previous calculations concentrated on the CEBEs of C, N, O, and F. This work extends the DFT investigation of CEBEs by dealing with cases in three groups of boron-containing molecules: hydrides, trihalides, and borane adducts.

The calculations were performed on over 20 test cases. The average absolute deviation (aad) between the results from the s-pvtz basis set and the experimental data is 0.25 eV. The aad for a quintuple-zeta basis set, tested on 17 of the cases, is 0.26 eV.

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Preliminary Results for the Interaction of Carbon Monoxide with Iron Surfaces using Planewave Methods.

Cary F. Chabalowski, Margaret M. Hurley, Gerald H. Lushington

US Army Research Laboratory
AMSRL-WM-BD
Aberdeen Proving Ground, MD 21005-5066 USA

A planewave DFT approach, with core electrons represented by pseudopotentials, is used to study the interaction of CO with the surface of iron. Preliminary structural and energetic data will be presented for the interaction of CO with the (111) and (100) surfaces of BCC iron. The calculations will show how many layers of iron must be allowed to relax to account for the interaction with CO, and the degree of relaxation that takes place in the of the surface layers. The effect of the iron surface on the bond length of CO is also of interest as a possible first step in the carburization process of the iron.

The Quadrature Discretization Method (QDM) in the solution of the Fokker-Planck and Schroedinger equations

Heli Chen and Bernie D. Shizgal
Institute of Applied Mathematics
University of British Columbia
Vancouver, British Columbia V6T 1Z4

There has been an increased interest in the solution of quantum mechanical problems with a discretization of the wavefunction in the Shroedinger equation(1). The traditional methods usually involve the expansion of the wave function in a suitable basis set, and the reduction of the differential equation to a set of algebraic equations for the expansion coefficients. The discrete approach in the solution of other differential and/or integral equations has been used by researchers in other fields, notably neutron transport, radiative transport, and computational fluid dynamics(2). In kinetic theory, a discretization method of solution of the linear Boltzmann equation was introduced by Shizgal(3) based on a new set of basis functions referred to as the speed polynomials.

This paper describes several applications of this discretization procedure referred to as the Quadrature Discretization Method (QDM). It is applied to the solution of the Schroedinger equation as well as the Fokker-Planck equation(4). The QDM employs a discrete grid which corresponds to the points for a quadrature based on some weight function defined on a given interval. The derivative operator is then represented as a finite matrix of dimension equal to the number of grid points. The QDM can be used to solve a large class of differential and integral equations and has also been applied to fluid dynamics problems(2). The main objective is to determine the weight function that defines the polynomial basis set and hence the grid points that provide optimum convergence in a given application. The QDM has the advantage that, (1) there are no matrix elements to evaluate and the representation of the Schroedinger equation and/or Fokker-Planck equation involves function evaluations, (2) the matrix representatives of the differential operators are symmetric and a variational principle applies, (3) the convergence of eigenvalues and eigenfunctions is extremely rapid with a judicious choice of the weight function, and (4) the eigenfunctions are determined at the points of a quadrature so that average properties can be determined efficiently.

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A COMPUTATIONAL STUDY OF THE PHOTODECOMPOSITION REACTIONS OF TRIFLUOROETHYLENE

Zekiye ÇINAR and Yüksel İNEL

Department of Chemistry
Yıldız Technical University, 80270 İstanbul-TURKEY

The photodecomposition kinetics of small organic molecules has been a subject of intense scientific research in the last decades due to the presence of different reaction channels producing a variety of reactive intermediates and primary products. Halo-olefins, especially chlorine and fluorine derivatives of ethylene are the most important compounds that have been studied experimentally.

In this project, the photodecomposition reactions of the excited trifluoroethylene molecule, C_2HF_3*, formed in the vacuum-UV photolysis of carbon suboxide, C_3O_2, in the presence of trifluoromethane, CHF_3, have theoretically been investigated with the intention of predicting the principal products. As already known, the primary photochemical products of the short-wavelength photolysis of C_3O_2 are free carbon atoms. Of the three atomic states of carbon produced, $C(^1D)$ atoms react with CHF_3 present through insertion into the C-H bond to produce the vibrationally excited C_2HF_3* molecule. This excited molecule, with a calculated energy content of about 158 kcal, either collides with other molecules present and stabilizes or decomposes through $\alpha\alpha$ or $\alpha\beta$ HF elimination to give difluorovinylidene, $:C_2F_2$, or difluoroacetylene, C_2F_2 as the major products.

The specific rate constants for the two decomposition reactions have been evaluated by means of the RRKM theory of unimolecular reactions. Ab initio molecular orbital calculations have been carried out at RHF/6-31 G* level of theory for the molecule and the two transition state structures. The stabilization/dissociation ratio has been calculated as a function of pressure with the assumption that the non-equilibrium energy distribution of C_2HF_3* molecules may be presented by the Gaussian distribution function. The relative concentrations of the principal products have also been calculated over the pressure range of interest.

Semiempirical Methods which Go Beyond the Minimal Basis Set

by John Cullen

Department of Chemistry
University of Manitoba
Winnipeg, Manitoba
Canada, R3T 2N2

Semiempirical molecular orbital methods are almost universally based on a minimal atomic orbital basis set representation even though it is well known such basis sets are inadequate for electron correlation energy calculations. To compensate for this, the effects of electron correlation are indirectly taken into account through the parameterization. On a more practical note, the extension of semiempirical methods to larger basis sets is computationally prohibitive due to the large numbers of parameters which must be optimized. We present a progress report on this latter problem which uses a diatomics in molecules (DIM) approach applied to the second quantized form of the ab initio molecular Hamiltonian. This results in the dropping of all 3 and 4 center atomic integrals. To approximately correct the resulting errors a supplementary empirically parameterized one electron operator is introduced. Using a double zeta + polarization valence atomic orbital basis for this semiempirical method calculated energies, equilibrium geometries, vibrational frequencies are presented and compared with the equivalent fully ab initio procedure at the Hartree Fock, MP2, CCSD, CASSCF and GVB levels of theory.

An Examination of the GVB Appoach Using an INDO Model Hamiltonian

by **John Cullen** and Michael C. Zerner*

Department of Chemistry
University of Manitoba
Winnipeg, Manitoba
Canada, R3T 2N2

Recently the GVB perfect pairing algorithm based on a coupled cluster ansatz was incorporated into the semiempirical Zindo program. The analytic gradients as well as first order density matrix have been derived and programmed. In addition to discussing the theory, we report and compare initial results of test calculations on several transition metal systems at various levels of theory, and with experiment.

*Permanent address: Quantum Theory Project, University of Florida, Gainesville, Florida 32611

Separation of Chiral Particles in an Enantiomeric Mixture

Bedamati Das, Natalie M. Cann

Department of Chemistry, Queen's University, Kingston, Canada.

The importance of chiral molecules lies in the role they play in biological as well as chemical processes. This work focusses on enantiomeric mixtures involving particles having a single chiral center. In particular we are interested in the properties of these enantiomeric mixtures and in strategies for their separation. To this end the application of molecular dynamics(MD) simulation based methods to model enantiomeric mixtures will be discussed. Mixtures which include a "discriminator" will be investigated in order to shed light on the mechanism of chiral discrimination.

Preliminary results for mixtures of model D- and L- alanine particles will be presented.

The Dynamics of Selective Solvation in Binary Solvents: An MD Study

Tyler J. F. Day and G. N. Patey

Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, Canada V6T 1Z1

Considerable work has been done over the years concerning the solvation dynamics of a newly charged solute particle immersed in a polar solvent. Of primary concern has been the rate at which the solvent can respond to the newly introduced field. In contrast, relatively little attention has been focussed on ion solvation in binary solvents. Recent simulation results for such studies will be presented, focussing on the dynamics of the solvent relaxation as well as on the equilibrium properties of the preferential solvation. A detailed study of the nature of the structural relaxation has shown that it occurs in two more or less distinct phases following solvent reorientation. There is an initial, rapid electrostriction phase as the solvent density about the solute increases. This is followed by a considerably slower redistribution phase by which the composition of the solvation shells undergoes change. This redistribution phase, as well as the final equilibrium structure, depends not only on the direct solute-solvent interactions, but also on solvent-solvent interactions and packing considerations. Results for both simple mixtures of Stockmayer solvents as well as more realistic systems, such as water/methanol and water/DMSO, will be presented.

Proposition for the acylation mechanism of serine proteases.

G. Dive, **D. Dehareng**

Centre d'Ingéniérie des Protéines, Institut de Chimie B6, Sart Tilman, B4000, Liège, Belgium.

This work proposes an *ab initio* study [1] of the hypothesis for a one-step acylation process of serine proteases [2], with one water molecule acting as the main catalyst reactant.

For the 11 increasing complexity models considered, the minimum and transition state conformations for the reaction are determined by full geometry optimization at the *ab initio* self-consistent field Hartree-Fock level within several basis sets, from MINI-1 to 6-31G and, for the smaller complexes, at the post-SCF MP2 level within 6-31G** basis set.

The related thermodynamical quantities are calculated for all the conformations.

The influence of the oxyanion hole stabilizer and of the dyad His57-Asp102 is quantified and a very good agreement is obtained with point mutagenesis [3].

The activation barrier is found in the range 15-18 kcal/mol.

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Applications of Computational Thermochemistry

David A. Dixon, David Feller, Kirk A. Peterson, Holger Dachsel, and Robert Harrison

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory[a], Battelle Blvd, P.O. Box K1-83, Richland WA, 99352

A clear revolution in science has taken place over the last two decades. This revolution is based on the utilization of high performance computers (now massively parallel) to solve the complex equations (such as the Schrodinger equation for electronic motion or Newton's equations of motion) which describe natural phenomena. Both software and hardware developments have contributed to this revolution. We will describe how high level computational chemistry can be used to predict molecular properties including heats of formation. The calculations are based on extrapolating CCSD(T) energies obtained from the correlation consistent basis sets, up through augmented quadruple zeta, to the complete basis set limit. Core/valence corrections were obtained from basis sets designed to recover such effects. Spin-orbit corrections are also made as are zero point energy corrections. We will discuss the accuracy of such calculations and their application to compounds including BH_3, B_2H_6, CF_2, CF_2O and CF_2H_2. In addition, we will discuss calculations on the region around the minimum of the potential energy curve of Cr_2 at the multi-reference configuration interaction (CI) level which included almost 1.3 billion configurations in the CI calculation. We will also describe the use of lower level calculations for predicting thermochemistry of use in the remediation of nuclear waste from defense production facilities.

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Electron-correlated polarizabilities of 87 five- and six-membered-ring azaboracycles

Robert J. Doerksen and Ajit J. Thakkar

Chemistry Department, University of New Brunswick, Fredericton, NB, Canada E3B 6E2

Ab initio second-order Møller-Plesset (MP2) perturbation theory calculations of static dipole polarizabilities are reported for cyclic molecules containing BH, CH, NH, N, and O. The uncorrelated Coupled Hartree-Fock (CHF) method overestimates the principal polarizability of 28 of the molecules. The ratio MP2/CHF varies from 0.8 to 1.1 for the average polarizability and from 0.7 to 1.2 for the anisotropy.

Replacing CH with N, or NH with O, in every case reduces the polarizability, though there is a fairly broad distribution of differences. By contrast, the corresponding BNH_2 for C_2H_2 substitution sometimes increases and sometimes decreases the polarizability.

Additive atom and bond polarizability models which are accurate to within a few percent are constructed for a larger set of 120 monocycles, including azines, azoles, oxazoles. The presence of boron causes scatter of the polarizabilities of isomers; hence the additive models of polarizability are less accurate than if only heterocycles containing CH, NH, N, and O are included.

NMR-Shieldings and Vibrational Spectra of small N-Heterocycles: Experimental versus ab initio calculated data.

A. Dokalik, W. Mikenda

Universitiy of Vienna
Institute for Organic Chemistry
Währinger Straße 38
A-1090 Wien
AUSTRIA

Ab initio calculated NMR (^{1}H, ^{13}C, ^{15}N) and vibrational (IR, Raman) spectroscopic data are presented for a series of N-heterocycles. The performance of different theoretical approaches for calculating spectroscopic properties is inspected by a comparison with corresponding experimental data, focusing on the agreement of spectral patterns and spectral trends.

GIAO NMR calculations were performed at several computational levels, including HF, B3LYP, and BLYP levels of theory, 6-31G(d,p) up to 6-311++G(2df,2dp) basis sets, and HF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) optimized geometries. In summary, the results obtained here confirm the results of a recent study of a series of aroyl compounds [1]. In particular it turned out (i) that the sequences of GIAO-BLYP calculated shieldings of ^{1}H, ^{13}C, and ^{15}N nuclei agree well with the experimentally ($CDCl_3$ and DMSO solutions) observed sequences (correlation coefficients $r > 0.99$), (ii) that GIAO-HF calculated shieldings of aromatic carbons and hydrogens suffer from systematic shortcomings, and (iii) that the choice of the level of theory for the geometry optimization has almost negligible influence (thus the computationally less demanding HF geometries seem to be quite suitable).

Vibrational spectroscopic data were calculated at the and HF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) levels of theory. Assignments of experimental frequencies were made considering theoretical and experimental frequency sequences and intensity distributions. Comparison between theoretical and experimental (CCl_4 and CS_2 solutions) data yields excellent agreement for B3LYP calculated data, whereas HF and MP2 data are less satisfying due to the well-known problems associated with a correct description of aromatic force fields [2].

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Interfacing relativistic and nonrelativistic methods.

Kenneth G. Dyall

Thermosciences Institute, NASA Ames Research Center, Mail Stop 230-3,
Moffett Field, CA 94035-1000, USA

An approach for incorporating relativistic effects at the all-electron level into nonrelativistic molecular calculations is presented. The formalism is based on the modified Dirac equation in which spin separation may be achieved, and on the equivalence of the nonrelativistic wave functions to the solutions of the Lévy-Leblond equation. Two principal approximations are involved in the development: the freezing of the Dirac negative energy states at the separated atom limit, and the definition of an atom-centered fine structure constant, which classifies the atoms as "relativistic" or "nonrelativistic". Results are presented for a number of test systems. The first approximation has negligible effect on molecular properties; the second gives small effects for light atoms, as expected.

THE SIXTEEN VALENCE ELECTRONIC STATES OF NITRIC OXIDE DIMER, $(NO)_2$

Allan L. L. East

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6.

Sixteen electronic states of nitric oxide dimer are investigated using various *ab initio* levels of theory and various orientations of the dimer. These are the states which arise from the mixing of the singly occupied π^*_{NO} orbitals of the monomers, and include all eight states which directly correlate to the $^2\Pi$ ground states of the monomers. Twelve of the sixteen states are significantly multiconfigurational in character, which cause incorrect state orderings at low levels of theory. At several plausible geometries, eight low-lying states are predicted (4 singlets and 4 triplets) within a 1 eV span, hence corresponding to excitations in the *infrared*, while the other eight states (6 singlets and 2 triplets) lie much higher in the far ultraviolet, and in the realm of numerous other electronic states. The results imply, but do not confirm, that the only potential minimum lying below the lowest dissociation asymptote is the cis-ONNO geometrical conformation of the $\tilde{X}^1A_1$ ground state.

The Multireference Relativistic Coupled Cluster Method: Some recent developments

Ephraim Eliav and Uzi Kaldor

School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

Different high-quality ab-initio approaches incorporating both relativistic and correlation effects to high-orders are discussed. The most reliable treatment of relativity starts from the first-principles four-component no-pair Dirac-Coulomb-Breit (DCB) Hamiltonian. For molecules, however, the four-component method is often too expensive, and we also consider one- and two-component approximations based on a non-singular transformation of the DCB Hamiltonian. Multireference correlation schemes presented include the Fock-space coupled-cluster (CC) method, equation-of-motion (EOM-CCSD) and many-body perturbation theory.

Calculations of energies (e.g. excitation and dissociation energies) and other properties (e.g. nuclear quadruple moments) of some heavy atomic and molecular systems are presented. A detailed study of the influence of nonadditive effects of relativity and electron correlation on atomic and molecular properties is provided.

Hybrid Quantum Mechanical and Molecular Mechanical Potentials for Studying Reactions in Proteins and in Solution

Martin J. Field, Patricia Amara, Celine Bret, Flavien Proust
and Aline Thomas

Laboratoire de Dynamique Moléculaire
Institut de Biologie Structurale — Jean-Pierre Ebel
41 Avenue des Martyrs
38027 Grenoble Cedex 1
France

Hybrid quantum mechanical (QM) and molecular mechanical (MM) potentials have proved to be powerful tools for the simulation of many processes in condensed phase systems and, as a result, they are an active area of current research. We highlight a number of developments that have been made in our laboratory to improve the accuracy of our hybrid potentials. These include the use of fluctuating charge potentials to account for polarization effects on the atoms in the MM region and a generalized hybrid orbital approach (in collaboration with J. Gao, SUNY, Buffalo) to model molecules with both QM and MM atoms. Application of these potentials, implemented in our QM/MM program, DYNAMO, will be illustrated with examples of simulations of different protein and solution phase systems.

Combined QM/MM Simulations of Chemical Reactions in Solution and in Enzymes

Jiali Gao

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14260

Abstract: In this paper, we discuss recent development and applications of combined quantum mechanical and molecular mechanical (QM/MM) potentials in simulation of chemical processes in solutions and in enzymes. The emphasis of this approach is on the treatment of the reactive region (e.g., the solute) with quantum mechanics, while the remainder of the system (e.g., the solvent) is represented by molecular mechanics. Consequently, combined QM/MM methods can synthesize both accuracy and computational efficiency for the study of chemical reactions in condensed phase. Here, we discuss factors that govern the accuracy of combined QM/MM simulations, including the treatment of QM/MM boundary, long-range electrostatic interactions, and mutual solute (QM) and solvent (MM) polarization. In addition the question of balancing computational accuracy and practicality in applications to biological systems will be addressed in the context of methods ranging from semiempirical models to ab initio molecular orbital and density functional QM/MM simulations. Examples of applications include nucleophilic substitution reactions in solution and a dephosphorylation process catalyzed by protein tyrosine phosphatases.

Oxidative degradation of radical-containing enzymes

James W. Gauld and Leif A. Eriksson

Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

It is now known that many enzymes contain radical centres, which play central roles in the functioning of the enzyme. In particular, the anaerobic enzyme Pyruvate-formate Lyase (PFL) contains a radical centre on a glycine amino acid, i.e., R_1—HN–$\dot{\mathrm{C}}$H–CO—R_2, within the enzymes acive site. This glycine radical is very stable. However, the exposure of PFL to an oxygenated solution, results in the destruction of the enzyme which breaks at the C—N bond of the glycine radical.

While much has been learnt, experimentally, about how oxygen interacts and reacts with biological radicals, in particular radicals of amino acids, the exact mechanisms are not fully understood. Due to the importance of such mechanisms, this is an unsatisfactory situation.

Theoretical methods of Quantum Chemistry can be used to give greater insight into the various possible mechanisms and their thermochemistry. We have employed density functional theory (DFT) methods to investigate the reaction of molecular oxygen (O_2), and related radicals, with two model amino acid radicals; the glycine radical ($H_2N\dot{C}HCOOH$) and the 'extended' glycine radical ($OHCNH\dot{C}HCONH_2$) model.

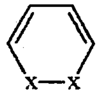
Recently, experimentalists have suggested an alternative pathway in which oxygen reacts with the glycine radical residue to form a peroxy radical (R_1—HN–C(H)O$\dot{\mathrm{O}}$–CO—R_2), which then reacts with a sulphur of a cysteine residue located nearby in the enzyme active site. Preliminary results of theoretical investigations of this mechanism will also be presented.

The Biradical Characters of 1,2-Dithiin, 1,2-Dioxin and Their Valence Isomers.

John D. Goddard[+] and Vladimir Pitchko[++]

[+]Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada, [++]Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada

1,2-Dithiin (X=S, 1) and its valence isomers (2-7) were studied by ab initio methods at the UHF level employing the guess=mix option to destroy symmetry. Solution for these systems obtained without destroying the α–β spin- symmetry displayed Hartree-Fock instabilities. Optimized geometries of all structures are minima (even the cZc-isomer (2) which according to previous work is a transition state). The biradical characters for all these structures were analyzed following the scheme of Yamaguchi. According to this scheme the 2-butenedithial isomers have significant singlet biradical character while 1,2-dithiin has only a small amount of biradical character. Proposals regarding the nature of the intermediates in the photolysis of 1,2-dithiin are made.



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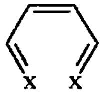

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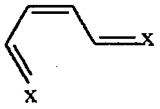

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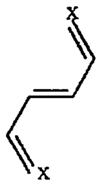

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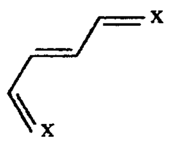

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An investigation of 1,2-dioxin (X=O, 1) and its valence isomers (2-7) was carried out at the UHF/6-31G*, 6-31G**, 6-311G*, 6-311G** levels and the biradical character analyzed as in the sulfur containing species.

SOLVENT EFFECTS ON CHEMICAL PROCESSES

MARK. S. GORDON

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
AMES, IA 50011

The role of solvents, especially water, in the nature of chemical processes is a critical area of current research. This talk will consider this role at several levels. The catalytic role of a small number of solvent molecules will be considered in several contexts, including the mechanism of formation complex silicon-oxygen cage compounds and proton transfer in the ground and excited states of biomolecules. This will be followed by a brief introduction of the effective fragment potential (EFP) model for solvation and the use of this method to study solvent effects on a variety of chemical processes.

Synchronization Defects and Transition to Turbulence in Spiral Waves

Andrei Goryachev and Raymond Kapral
Chemical Physics Theory Group, Department of Chemistry,
University of Toronto, Toronto, ON M5S 3H6, Canada

The spatio-temporal self-organization is studied in chemical media whose local dynamics is governed by nonlinear autocatalytic reactions. We demonstrate that spiral waves typical of excitable and ordinary period-1 oscillatory media can also exist in systems whose local dynamics is represented by chaotic or complex periodic oscillations. A macroscopic rotating spiral wave arises as a result of self-organization of local concentration oscillations into a synchronized pattern that involves the whole medium. The rotational symmetry of such waves is broken by the presence of synchronization defect lines where the phase of the local oscillation changes by multiples of 2π. The line defects join spiral cores of the waves with the opposite topological charge or form closed loops acting as interfaces between domains of near synchronization where the local phase changes continuously but experiences sudden jumps when a domain boundary is crossed. The dynamics of such domains plays central role in the transition to spatio-temporal chaotic regimes which can be characterized as defect-line mediated turbulence. We present detailed description of period-doubling bifurcations and subsequent transition to turbulence observed in these media as the bifurcation parameter is varied.

Electronic g–tensors of molecules. Significance of electron correlation.

F. Grein, P.J. Bruna and G.H. Lushington.

Department of Chemistry, University of New Brunswick, Fredericton, NB E3E 6E2 Canada

Previously methods have been developed to calculate g–tensors of molecules using perturbation theory based on ab initio multireference configuration–interaction (MR–CI) wavefunctions [1–5].

The perturbation operator contains (i) the spin–Zeeman term, (ii) the relativistic mass correction, (iii) the one and two–electron gauge correction, (iv) the spin–orbit interaction and (v) the orbital Zeeman interaction.

Applications to small molecules such as CO^+, NO_2, H_2O^+, MgF and others show that the large Δg component ($\Delta g = g - g_e$) often changes significantly when going from an uncorrelated (ROHF) to a correlated (MR–CI) treatment. For example, Δg_{yy} of NO_2 (the molecule is placed in the yz plane) changes from the ROHF value of –6597 ppm to the MR–CI value of –10296 ppm, compared with an experimental result of –11700 ± 500 ppm, using a (10s6p4d/5s3p2d) basis set with additional Rydberg functions.

Results obtained recently for H_2CO^- ($H_2CO{\cdot}Na$) [6], H_2COH, C_2Li, C_2Na, O_3^-, O_3Li, O_3Na, O_2^-, O_2Li, O_2Na and OLi, ONa will be presented. It is shown that the observed Δg values of C_2Li and C_2Na do not correspond to the ground state but to the 1^2B_1 excited state of these systems.

In both $H_2CO{\cdot}Na$ and H_2COH, the g–tensors are dominated by $\sigma\pi^*$ and $n\pi^*$ excited states. For the O_3^- systems, Δg_{yy} is governed by one $\sigma\pi^*$ state, and Δg_{zz} by two $b_2\pi^*$ states.

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Knowledge-based Structure Prediction with the Hierarchical Algorithm

Pierre-Jean L'Heureux, Alexandre Lemak, Geneviève Dufresne, and **John R. Gunn**

Département de Chimie
Université de Montréal
C.P. 6128, Succ. Centre-ville
Montréal, Québec H3C 3J7
and
Centre de Recherche en Calcul Appliqué
5160 boul. Décarie, bureau 400
Montréal, Québec H3X 2H9

Applications of the hierarchical algorithm will be discussed which make use of sequence-specific information, both experimental and theoretical, to supplement generic structural models and scoring functions. The hierarchical algorithm uses a combined Monte Carlo and genetic procedure to carry out a simulated-annealing minimization. The trial moves are selected from pre-screened lists of segments which in turn evolve during the simulation in a nested fashion using lists of smaller segments as trials. Segment lists are selected based on geometric compatibility with existing higher-level structures as well on local propensities. Additional sequence-specific information is added at both the local level, in the screening of trial segments, and at the global level, in additional terms added to the scoring function. Experimental data from NMR spin coupling and chemical shifts are used to provide estimates of backbone dihedral angles which can be used to directly bias the construction of segments. Non-local distance constraints from NOE cross peaks are used to modify the contact potential in cases where the data is sparse or ambiguous. At the theoretical level, local constraints are also derived from a database of homologous fragments found in known structures, and sequence alignment and threading calculations are used to predict likely contacts and provide global folding templates. A theoretical model of sidechain conformational flexibility is also used to modify the residue contact potentials, with likely sidechain rotamers predicted from observed correlations with backbone conformation. Selected results will be shown to illustrate the implementation and testing of these techniques.

Ab initio Calculation of the Electronic Structure of Cadmium Sulfide Cluster Fragments Prepared with Stabilizing Thiolate Ligands

V.S.Gurin

Physico-Chemical Research Institute, Belarusian State University, Leningradskaja str., 14,
220080, Minsk, BELARUS; E-mail: gurinvs@usa.net

Cadmium chalcogenide clusters can be successfully synthesized in solution with the protective ligands (thiols, phenylphopsphines, etc.), and their properties are extrapolable from those of small CdS particles due to the quantum size effects. The latter possess the bulk-like lattice while the protected clusters can have only a core from the sphalerite or wurtzite lattice, the dangling bonds, ligands atoms, and non-perfectly coordinated atoms occur. Thus, the direct extrapolation of semiconductor properties taking into account quantum-size effects is not adequate. In order to study theoretically properties of such clusters a quantum chemical approach is worthwhile which allows to consider an arbitrary geometry with deviation from the perfect bulk lattices. Semiempirical calculations were carried out recently by the author for similar clusters, and the reasonable trends in the variation of their properties were established. Some few atom clusters (Cd_xS_y, $x+y \leq 10$) were calculated also at the all-electron RHF SCF level.

In the present work we consider a series of the clusters being fragments of the well characterized $Cd_{17}S_{28}$-R (**I**) clusters [1]. They are obtained by step-by-step building of **I** with conservation of T_d symmetry and have the content: CdS_4, $Cd_{13}S_4$, $Cd_{13}S_{16}$, $Cd_{17}S_{16}$. The ligands were simulated by hydrogens. MO LCAO RHF calculations were carried out with ECP basis set (including d-orbitals of Cd) and the symmerty-constrained geometry optimization. Results show no simple monotonous variation of the properties in this series. The largest members of the series have the value of HOMO-LUMO difference (allowed dipole transition) correlated with experimental values of the first optical transition [1] (5.03 and 5.60 eV for $Cd_{13}S_{16}$ and $Cd_{13}S_{16}H_{12}$, respectively). It is noticeable the shortening of Cd-S interatomic distance for the central Cd-S_4 core, while another ones (e.g., 2.455Å in $Cd_{13}S_{16}$) are close to that determined crystallographically. Effective charges both at Cd and S atoms are rather large that can provide a 'chemical activity' of these species with further intercluster binding.

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Density Functional Theory Study of Water Adsorption on the MgO (001) Surface

Maciej Gutowski[a*], John E. Jaffe[b], Zijing Lin[b], J. Snyder[b], Jeffrey A. Nichols[a], M.I. McCarthy[a], G.K. Schenter[a], and Anthony C. Hess[b]

[a]*Theory, Modeling, and Simulations*
[b]*Materials and Chemical Sciences*
Pacific Northwest Laboratory, Richland, Washington 99352

The interface of water monolayer and the MgO (001) surface was studied within the framework of density functional theory (DFT) with local and gradient corrected functionals and a polarized double-zeta quality basis set. The initial equilibrium positions of water molecules were determined in classical molecular dynamics simulations and final distances of water molecules from the surface were optimized in DFT calculations. For different water coverages we found significant differences between the LDA and gradient corrected predictions, with LDA leading to larger water binding energies and shorter separations between interacting slabs. The energy (per one water molecule) required to separate the water and MgO slabs amounts to 18.6, 6.2, and 9.3 kcal/mol for the LDA, Becke-Lee-Yang-Parr, and the Perdew-Burke-Enzerhof functionals, respectively, and the energy required to break the water net is 6.4, 4.0, and 4.8 kcal/mol for the respective functionals. The unit cell for the 2/3 coverage contained 24 atoms, periodic orbitals were built from 504 atomic orbitals per unit cell, and charge density was approximated with 1116 fitting functions per unit cell. We have developed a parallel version of the DFT code for periodic systems and the current application was performed on 128 nodes of the SP IBM computer with the efficiency of ca. 80 %.

[*] On leave from Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland.

Improving the prediction of long-range properties within density functional theory

Nicholas C. Handy and David J. Tozer

Department of Chemistry
University of Cambridge
Cambridge CB2 1EW

Conventional continuum exchange-correlation functionals – i.e. those which do not include any fraction of exact orbital exchange – poorly describe properties that are sensitive to the asymptotic regions of molecules. Static polarisabilities are generally overestimated, while electronic excitation energies, computed as the poles of the frequency-dependent polarisability, are severely underestimated for excitations to Rydberg states. These inadequacies are closely related to errors in the virtual Kohn-Sham eigenvalues, which arise due to a fundamental deficiency in the exchange-correlation potentials of continuum functionals. Although such potentials correctly average over the exact integer discontinuity in energetically important regions, they fail to do so asymptotically because they vanish. A simple procedure is described which corrects this asymptotic deficiency for any continuum functional $E_{xc}[\rho]$. In the procedure, Kohn-Sham calculations are performed using a modified potential which equals the conventional potential $\frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$ in energetically important regions, but which asymptotically behaves in the appropriate non-vanishing average manner $-\frac{1}{r}+C$. The resulting orbitals and eigenvalues are used to determine static polarisabilities and excitation energies for a variety of molecules. Polarisabilities are of MP2 quality, while excitations to Rydberg states are predicted as accurately as those to the valence states. An understanding of Density Functional Theory for the H atom is presented. Forty-eight excitation energies for benzene are presented which have a mean absolute error of 0.15 eV.

STRUCTURE-ACTIVITY RELATIONS FOR THE GAS-PHASE REACTIONS OF HYDROXYL RADICALS WITH ALIPHATIC ALCOHOLS

Arzu HATİPOĞLU, Zekiye ÇINAR

Department of Chemistry
Yıldız Technical University, 80270, İstanbul-TURKEY

The reactions of hydroxyl radicals with alcohols have gained considerable attention in the past few years, because of their increasing importance in atmospheric, combustion as well as in biochemical processes. However, experimental kinetic data on these reactions are available only for a limited number of alcohols. Thus, there is a need to find predictors in order to determine the rates of the reactions of OH radicals with alcohols whose reactions have not been investigated.

In this project, the kinetics of the reactions of OH radicals with straight chain and cyclic aliphatic alcohols with one to five carbon atoms have been examined theoretically with the intent to determine the mechanisms of H-abstraction and the rates of the reactions. The optimum geometric parameters, electronic and thermodynamic properties of the reactants, products and the transition state complexes have been calculated by using semiempirical AM1 and PM3 methods. Based on the results of the quantum mechanical calculations, the rate constants of the reactions have also been calculated by means of the Transition State Theory.

As a result; two different QSARs expressing the logarithms of the rate constants,for the most probable routes of H-abstraction reactions of alcohols with OH radicals, in terms of the energies of the highest occupied molecular orbital, charge densities, vibrational frequencies and dissociation energies of carbon-hydrogen bonds have been derived. A kinetic model has also been proposed for the reactions of OH radicals with aliphatic alcohols in accordance with the calculated rate constants and the electron densities of the atoms in the alcohol molecules.

This project was supported by the Yıldız Technical University Research Fund,

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A Quantum Chemical Investigation of Hydrated Halide Adsorption on the Cathodic Al(111) Surface

Visvaldas Kairys and **John D. Head**

Department of Chemistry
University of Hawaii
Honolulu
Hawaii 96822, USA

Recent *in situ* experiments with techniques such as scanning tunneling microscopy and atomic force microscopy have greatly added to our understanding of the fundamental atomic interactions taking place at electrode surfaces. We will provide additional information by presenting results of cluster calculations which simulate water, fluorine and iodine adsorption on the cathodic Al(111) surface. We determine the water to be only weakly adsorbed on the negatively charged Al clusters with the water H atoms being closest to the metal surface. For the halides, in line with gas phase adsorption experiments and other calculations, we find that fluorine is much more strongly bound to Al clusters than iodine. However, from electrochemical experiments, the iodide ion is well known to readily specifically adsorb at cathodic electrodes, whereas the fluoride ion does not. In our poster we will present a possible explanation for this electrochemical trend based on calculations with a halide ion and one or more water molecules coadsorbed on negatively charged Al clusters.

New Electronic Structure Methods for Large Molecules and Bond-Breaking

Martin Head-Gordon

Department of Chemistry
University of California, Berkeley, and,
Chemical Sciences Division,
Lawrence Berkeley National Laboratory
Berkeley, CA, 94720 USA.

In this talk, I will discuss topics from the following list of current interests:

(1) The problem of achieving linear scaling algorithms for systems with significant delocalization. In metallic, or small gap systems, the range of the density matrix is very large and existing sparsity-based linear scaling methods fail.

(2) Overcoming the unphysical computational complexity of wavefunction- based electron correlation methods. Local electron correlation methods show great promise, and I have recently introduced a new tensor-based formulation of many-body theory that permits new local models using nonorthogonal occupied and virtual orbitals.

(3) The development of new electron correlation techniques which are capable of describing bond-breaking, diradicals, and other problems for which conventional single reference theories fail. I wish to overcome the limitations of existing multireference methods, which are prohibitive computational cost, and/or the need for case-by-case customization.

Development and application of analytical energy gradient methods in correlated crystal orbital theories

So Hirata and Suehiro Iwata

The Graduate University for Advanced Studies and Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

Analytical formulas for the first and second derivatives of electronic energy with respect to nuclear coordinates are essential in studying the structures, vibrational frequencies, and other properties of polymers on the basis of *ab initio* crystal orbital theory. Recently we have implemented the analytical-gradient method in density functional and hybrid Hartree–Fock (HF)/density functional crystal orbital theories [1], and the analytical-second-derivative method in HF crystal orbital theory [2]. In this conference, we present (1) the formulas and computer implementation of the analytical energy gradients of the second-order Møller–Plesset (MP2) perturbation energies of polymers, and (2) the vibrational analyses of an infinite hydrogen fluoride polymer based on HF and density functional crystal orbital theories.

(1) The spin-restricted formulas for the analytical gradients of the MP2 energies are presented within the crystal orbital scheme. The coupled perturbed Hartree–Fock equation is solved iteratively using the atomic-orbital-based algorithms. The MP2 energy and its gradient contributions are evaluated by the disk-based algorithms with the aid of the two-particle density matrix. Illustrative calculations are presented on all-*trans* polyacetylene.

(2) Optimized structural parameters, binding energies, and vibrational frequencies are obtained for an infinite zigzag hydrogen-bonded chain of hydrogen fluoride molecules using the HF, Becke–Lee–Yang–Parr, and Becke3–Lee–Yang–Parr approximations with the 6-311++G(d,p) basis set. Chain-length dependence of these quantities is examined by carrying out the molecular orbital calculations on hydrogen fluoride clusters in the linear configurations. The effects of electron correlation on the cooperativity of the hydrogen bonds and the assignment of the observed infrared and Raman bands of crystalline hydrogen fluoride are discussed on this basis.

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Penning ionization from attractive superexcited states: $H_2O + He^* \rightarrow H_2O^+ + He + e^-$.

Toshimasa Ishida

Applied Sciences, Faculty of Engineering, Shizuoka University, 836, Ohya, Shizuoka 422-8529, Japan

Superexcited states have been much more accessible than ever with the development of synchrotron radiation and lasers. The states can lead to autoionization because the states are embedded in the ionization continua. Penning ionization is one of these autoionization processes. In the gas phase, Penning ionization is described by the following process:

$$\mathrm{M} + \mathrm{A}^* \rightarrow \mathrm{M}^+ + \mathrm{A} + e^-, \qquad (1)$$

where M is the target molecule, and A* is an excited species. The experiments of Penning ionization electron spectroscopy include a type of transition-region spectroscopy because the ionization can occur at any distance between M and A.

In recent years, we have been studying Penning ionization theoretically[1-7]. In this presentation, we will show the result of the calculations for the Penning ionization system[3,4,7]

$$H_2O + He^*(2^1S, 2^3S) \rightarrow H_2O^+(^2B_2,\ ^2A_1,\ ^2B_2) + He + e^-. \qquad (2)$$

Ab initio calculations were performed for the above system using the Feshbach projection operator method to evaluate the potential energy surfaces (PES) of the resonance state and the partial widths for individual partial ionization. Configuration interaction calculations with single and double excitations were performed using a TZP basis set augmented with diffuse functions on He. An attractive well near the oxygen lone pairs was found both for the triplet and singlet entrance channels, whereas the region outside of the OH bonds is repulsive. The well for the singlet entrance channel is deeper but smaller than the corresponding well for the triplet channel. The partial widths reflected the electron distribution of the molecular orbital from which an electron is ejected in the ionization.

Quasiclassical trajectory calculations were performed at H_2O rotational temperatures of 300, 150, and 25 K based on the PES and the widths evaluated. When rotational temperature decreases, ionization cross section increases for both the systems. This is because more trajectories are trapped in the attractive region, and the trapped trajectories results in considerable ionization. Since the partical width for the ionization into the $^2A_1$ state is larger at the trapping region, the $^2A_1$ ionization is predominant. The trajectories on the singlet surface were drawn into an attractive H_2O lone pair region less strongly with decreasing rotation frequency than the trajectories on the triplet surface. Fewer trajectories ionize at lower energy for the singlet surface than for the triplet surface. These two results are due to the long-range barrier and the smaller well of the resonance PES for the singlet surface.

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Ab initio molecular dynamics simulations of the interaction of NO_2^+ with clusters of three and four water molecules

Yasuyuki Ishikawa and R. C. Binning, Jr.
Chemistry Department, University of Puerto Rico, San Juan, PR 00931-3346 USA

Ab initio molecular dynamics (MD) simulations of the interaction of NO_2^+ with clusters of three and four water molecules have been performed. The studies have been undertaken to gain an understanding of the mechanism of

$$NO_2^+ + (H_2O)_n \rightarrow HNO_3 + H_3O^+(H_2O)_{n-2}$$

in which n = 3, 4. The process is believed to be a step in the interconversion of nitrogen pentoxide and nitric acid,

$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$

This conversion is important in the chemistry of the stratosphere. Each of the nitrogen-containing species is a significant trace compound, and both play a role in the cycle of stratospheric ozone depletion. HNO_3 in the troposphere is also a major determinant of the acidity of rainfall.

Several experimental studies of the fragmentation of $NO_2^+(H_2O)_n$ (n = 1–5) clusters by collision and by photodissociation have been performed. The results for clusters containing four and five waters seem to agree. An HNO_3 unit seems to form in them and be ejected as the cluster fragments. With NO_2^+ one- or two-water clusters, there is no evidence that HNO_3 is formed internally, and H_2O is the major evaporation product when the cluster fragments. It is with $NO_2^+(H_2O)_3$ that the results are so far inconclusive, one recent study indicating that HNO_3 formation in the cluster is of minor importance, whereas another seems to indicate that it is quite significant. The discrepancy has engendered a situation in which a theoretical study of the detailed mechanisms of interaction in such clusters can potentially yield valuable insight.

We report on a number of direct molecular dynamics trajectories of $NO_2^+(H_2O)_{3,\,4}$, showing how HNO_3 and $H_3O^+(H_2O)_{1,\,2}$ form. We are able to show, in analyzing the disposition of vibrational energy, under what conditions the clusters will fragment by evaporation of HNO_3.

STRUCTURES OF WATER CLUSTER AND METAL-WATER CLUSTER ANIONS, AND PHOTODISSOCIATION DYNAMICS OF Ar_n^+

Suehiro Iwata

Institute for Molecular Science, Okazaki 444-8585 Japan

1) Two types of structures have been discussed for water cluster anions, $(H_2O)_n^-$, $n \geq 2$. One is the internal state, in which the excess electron is localized inside the cluster. Another is the surface state, often called dipole bound anion. It has been believed that small cluster anions have a dipole-bound excess electron. Recently, we have found a dimer anion in which an excess electron is confined in two water molecules facing each other [1]. We have extended the study for trimers and tetramers, and found a few internal type anions. as well as the dipole bound trimer anion recently reported [2]. The uniqueness of these internal type anions is that there are no hydrogen bonds among water molecules. The electron cloud binds the water molecules. In terms of total energy, the dipole bound anion is the most stable because of the hydrogen bonds, but its vertical detachment energy (VDE) is smaller than the internal type anions. The internal type anions are possible candidates of the counter ion of alkali metal cation M^+ in the clusters of $M^+(H_2O)_n^-$.

2) Using the DIM hamiltonian and Tully's MDQT (molecular dynamics with quantum transitions), we follow the photodissociation processes of Ar_n^+ (up to n=27). The size- and photon-energy-dependence of the decay processes are examined. It turned out that the initial photoexcited state exhibits a gaussian-like decay, which is followed by an exponential decay to reach the ground state. Most of the evaporation events of neutral argon atoms proceed on the ground state surface.

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Structure and Phase Transitions in CO Adsorbed on Insulator Surfaces (NaCl, LiF, MgO)

M.R. Goldsmith, **D.B. Jack**, A. Sallabi, and N.-T. Vu

Dept. of Chemistry and Biochemistry, Concordia University
1455 de Maisonneuve Blvd. W., Montréal, QC, H3G 1M8, CANADA

A set of Monte Carlo simulations of CO molecules adsorbed on the (001) face of NaCl, LiF, and MgO crystals are presented and compared with the experimental work of other groups. In the case of CO/NaCl(001) it is experimentally known that a monolayer of CO molecules undergoes a phase transition at a transition temperature of T_C=35 K. Below T_C an ordered p(2×1) phase is formed which transforms to a disordered p(1×1) phase above T_C . Monte Carlo simulations show that the order phase has a "spin flop" structure where molecules are tilted by 27° from the surface normal, in agreement with experiment, and have an antiferroelectric structure within the plane of the surface. Above the transition temperature of 35 K the antiferroelectric ordering disappears although the molecules remain in a tilted state indicating a 2-D order-disorder type transition. An analysis of the temperature dependence of the order parameter, heat capacity, and susceptibility indicates the transition is of the continuous type with non-universal critical exponents. There is evidence of an additional transition at a still higher temperature which might be of the Kosterlitz-Thouless (K-T) type. These simulations also predict that a similar phase transition is possible in the CO/LiF(001) system where the ordered state forms a p($2\sqrt{2}\times\sqrt{2}$)R45 herringbone structure. These systems are thought to exhibit a crossover in their critical exponents from Ising to K-T type behaviour. The CO/MgO(001) system is found to form a stable *c*(4×2) monolayer phase at temperatures below 40 K. In the range of 40 - 50 K the layer becomes unstable and expels molecules from the monolayer. The remaining molecules lose their long-range order, although small regions with p(3×2) and p(3×4) structures can form.

Extracting the Current Density from Experiment

Dylan Jayatilaka

Department of Chemistry, The University of Western Australia,
Nedlands 6009, Australia

This paper is concerned with modelling the (often ignored) counterpart to the electron density—the current density. Although the effects of the current density can be measured using the polarised neutron diffraction (PND) technique, it has never been possible in the past to completely reconstruct the current density vector field from the PND experiment.

Using a constrained minimisation technique [1, 2], a (complex) "experimental" wavefunction will be extracted from PND diffraction data for the $CoCl_4^{2-}$ ion within the Cs_3CoCl_5 crystal. From this experimental wavefunction I will display pictures of the current density in this system. I believe that they will be the first pictures of an experimentally derived total current density in any system.

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Ab initio calculations of the Cotton–Mouton effect for CO_2, N_2O, OCS and CS_2

Dan Jonsson, Patrick Norman[1], Antonio Rizzo[2],
Sonia Corriano[2], Hans Ågren[1]

San Diego Supercomputer Center
9500 Gilman Drive, MC 0505
La Jolla, CA 92093-0505, USA

The Cotton-Mouton effect is the magnetic field induced birefringence of a gas subjected to a strong external magnetic field. The induced anisotropy of the refractive index is proportional to the square of the magnetic field through the so-called Cotton–Mouton constant.

In the calculations, the effects of basis set, gauge origin dependence, and correlation have been studied. Comparison with experiment is also made with emphasis on the temperature independent part of the Cotton-Mouton constant (relating to the cubic response function), which is very hard to determine accurately experimentally.

All calculations (the first for these molecules) have been performed using the linear, quadratic and quadratic response functions for SCF and CASSCF wavefunctions as implemented in the DALTON[3] program.

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[1] Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

[2] Istituto di Chimica Quantistica ed Energetica Molecolare, Consiglio Nazionale delle Ricerche, Via Risorgimento 35, I-56126, Pisa, Italy

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Uniform Semiclassical Treatments for Time-Independent and Time-Dependent Wave Functions

Kenneth G. Kay

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel 52900

We report progress on two fronts toward the development of computationally convenient and accurate semiclassical approximations for time-independent and time-dependent wave functions.

We develop a novel, globally uniform semiclassical treatment for energy eigenstates and apply it to a multidimensional system. The adiabatic switching method is used to obtain various quantities that enter the semiclassical expression. The method is shown to be capable of producing accurate wave functions for both regular and mildly chaotic states – often, from a single classical trajectory. Although the present theory resembles the Frozen Gaussian Approximation (FGA), it is a true semiclassical approximation and is found to yield wave functions that are significantly more accurate than those obtained from the FGA for all states examined.

One, often inconvenient, restriction shared by the above treatment and related semiclassical initial value methods for dynamics is the requirement that the system be described in terms of Cartesian coordinates. We show how to generalize these treatments so that they can be applied to other coordinates as well. Test calculations demonstrate the usefulness and accuracy of these generalizations.

COMBINATION OF MONTE CARLO SIMULATED ANNEALING AND RISM THEORY FOR ANALYZING CONFORMATIONAL STABILITY OF PEPTIDE IN SOLVENTS

Masahiro Kinoshita, Yuko Okamoto, and Fumio Hirata

Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, JAPAN

The first-principle prediction of tertiary structures (conformations) of proteins in solvents from their primary structures is one of the most challenging problems. As a contribution to research for solving this problem, we report results of the first attempt to combine the Monte Carlo simulated annealing (MCSA), a powerful conformational sampling technique, and the reference interaction site model (RISM) theory, a statistical-mechanical approach for molecular fluids. In solvents the key function is the total energy defined as the sum of the conformational energy and the solvation free energy, and the RISM theory is employed to calculate the latter. The combination has been made possible by developing an algorithm for solving the large set of full RISM equations, which is robust and orders of magnitude faster than a conventional one (we note that no approximate treatment is employed to accelerate the RISM calculation). Starting from an initial conformation given, our computer program samples many conformations in accordance with the MCSA technique, and then finds the conformation with the minimum total energy. Met-enkephalin (Tyr-Gly-Gly-Phe-Met) in the two different solvents, the SPC/E water and a simple, repulsive-potential system, are considered, and several different conformations are tested as the initial ones.

In water the solvation free energy varies greatly from conformation to conformation, while in the simple solvent it remains roughly constant against conformational changes. In water most of the conformations with larger solvation free energies are strongly rejected and the number of probable conformations is drastically reduced, which is suggestive that stable conformations are reached far more rapidly than in gas phase and in the simple solvent. This result is important in the following two respects: water plays essential roles in stabilizing particular conformations of peptides; and in water the number of conformations to be sampled in simulations is drastically reduced, which could remove computational bottlenecks expected for much larger polypeptides or proteins. The stable conformations obtained in water are quite different from those in gas phase and in the simple solvent. Those in water are characterized by almost fully extended backbone structure with large fluctuations in side-chain structure, which is in qualitative accord with the result from the recent nuclear magnetic resonance experiment. The result for C-peptide (Lys-Glu-Thr-Ala-Ala-Ala-Lys-Phe-Leu-Arg-Gln-His-Met) will also be described in the talk.

THEORETICAL STUDY OF THE $OH^{-}(H_2O)_n$ SYSTEM

N. Turki[1,2], A. Milet[1], A. Rahmouni[3,1], O. Ouamerali[2], R. Moszynski[1,4],
E. Kochanski[1,4], P.E.S. Wormer[5]

1. UMR 7551 CNRS/ULP, Laboratoires de Chimie Quantique et Chimie Théorique, Institut Le bel, Université Louis Pasteur, B.P. 296, 67008 Strasbourg-Cedex, France, Email : kochansk@quantix.u-strasbg.fr

2. Université USTHB, Alger, Algérie; 3. Ecole Normale Supérieure de Saïda, Algérie; 4. University of Warsaw, Poland; 5. University of Nijmegen, Netherlands.

The structure and energetics of the anionic $OH^{-}(H_2O)_n$ clusters have been investigated using various theoretical approaches. In particular, the nature and importance of the three-body interactions in the clusters of the hydroxide ion with water molecules have been studied by several *ab initio* quantum-mechanical methods. For the dimer and trimer, benchmark calculations have been done at the MP4 and CCSD(T) levels within the scheme of the supermolecule model. They have been compared with the results of (semilocal) DFT calculations and with *ab initio* symmetry-adapted perturbation theory (SAPT) calculations. The latter approach allows a decomposition of the interaction energy into contributions with clear, partly classical, partly quantum-mechanical interpretation, such as electrostatics, exchange, induction, dispersion and exchange-induction/exchange-dispersion cross effects.

The SAPT decomposition has been applied to characterize the nature of the three-body interactions for various geometrical configurations of the $OH^{-}(H_2O)_n$ cluster (n=2, 3, 4, 10) with water molecules located either in the first or second solvation shell. In all cases the induction term is dominant, but is partly canceled by the first-order exchange energy, and the second-order exchange-induction and exchange-deformation effects. This suggests that the induction contribution is not a reliable approximation to the Hartree-Fock interaction energy. The dispersion and exchange-dispersion terms can be either negligible or significant depending on the geometry considered. This shows that the construction of simple analytical models for the three-body interaction potential of $OH^{-}(H_2O)_n$ may be highly nontrivial. For $OH^{-}(H_2O)_2$ the three-body energy represents only 5-7% of the pair interaction energy at the Hartree-Fock level, but can reach as much as 22.6% for $OH^{-}(H_2O)_4$.

Chaotic and Regular Dynamics of Isomerization Reaction of Ar_6 Cluster
-Origin of Collective Motions & Dividing Surface free from Recrossing Problem-

Tamiki Komatsuzaki and R. Stephen Berry

Department of Chemistry, The University of Chicago,
5735 S. Ellis Ave. Chicago, IL 60615, USA

The saddle crossings are one of the fundamental processes in chemical reactions, relaxation dynamics, phase transition of finite systems, and the other phenomena involving the structural change of systems. In the present study we scrutinize the saddle crossings' phase space structure of Ar_6 by using our new method based on Lie canonical transformation theory. Our purposes are to provide the fundamental origin of collective motions in complex atomic/molecular systems, and to gain a fundamental physical condition to yield a dividing surface free from the barrier recrossing problem, which is one of the central problems of (classical) transition state theories.

We show that, at small total energy above the saddle point energy, almost actions are found to maintain approximate invariants of motion along the saddle crossings and barrier *re*crossing motions observed over a *naive* dividing surface in the configurational space are "rotated away" to *no-return single* crossing motions over a dividing surface newly defined in the phase space. As the total energy increases, some modes mix due to the near-comensurability of their fundamental frequencies and the saddle crossings are changed from regular to chaotic dynamics topologically. However, we found that the action associated with the reactive mode tends to maintain the approximate invariant of motion along the saddle crossings in a wide range of energy, while no approximate invariants of motion could exist with the other non-reactive modes, and a dividing surface free from the barrier recrossing problem could be extracted from the phase space. We discuss the origin and the implications of the analytical hyperbolic coordinate on "collectivity of constituent atoms" and "chemical reaction kinetics".

Structure and spectroscopy of the cobalt substituted lactamase from *bacteroides fragilis*

H.Gilson and M.Krauss, CARB, Rockville, MD USA

Metallo-β-lactamases hydrolyze the lactam ring in antibiotics rendering the antibiotic ineffective. Two experimental studies, x-ray and spectroscopy of the cobalt substituted enzyme, did not agree on the overall coordination number of the two zinc atoms at the active site. Ab initio calculations of the spectra of models of the active site show that assumptions normally made correlating the spectra of the metal substituted protein to the concentration of protein are not in agreement with the theoretical predictions. Empirical rules used in the interpretation of the cobalt spectra to determine the coordination number are also found not strictly reliable for the ionic ligands often found at metal active sites.

The inherent transition energies and intensities for each isolated metal center and the bi-metallic active site are calculated by multi-configuration self-consistent-field (MCSCF) methods. One center, having three histidine ligands, resembles the active site of carbonic anhydrase (CA), while the other is essentially five-coordinate with one histidine, aspartate, and cysteine ligand inaddition to a water and the bridging hydroxyl anion. Comparable visible transition energies are predicted for both sites but the calculated intensities suggest that the CA site dominates. The presence of a cysteine does not enhance the visible transitions from the five-coordinate site. At least seven ligand to metal charge transfer (LMCT) transitions are predicted from the cysteine ligand to the open cobalt d-orbitals. The lowest energy transition, which is usually attributed experimentally to the entire LMCT transition, is assigned to the observed 330nm absorption. However, the intensities of the higher energy LMCT transitions are predicted to be much higher. These transitions are in the range where the tryptophan residues will absorb and will alter any correspondence between absorption at 280nm and the concentration of protein.

Crystallization of Molecular Liquids: Mechanisms and Techniques

P.G. Kusalik

Department of Chemistry, Dalhousie University, Halifax, N.S., B3H 4J3
Canada

Both the homogeneous nucleation and heterogeneous growth of a crystal from its melt are important physical processes, yet a detailed understanding of these processes at the microscopic has remained elusive. Computer simulation offers a very powerful tool with which to probe the microscopic mechanisms, both the structure and dynamics, of homogeneous nucleation and of heterogeneous crystallization. The first reports of the successful crystallization of molecular liquids in computer simulations have only recently appeared in the literature. In this paper I will begin by briefly reviewing the crystallization of molecular liquids, some of the important issues, results of some of the attempted simulation studies, and some key experimental data. I will then discuss our own success with computer simulations of the (homogeneous) crystallization of water and carbon dioxide. The techniques employed in our molecular dynamics simulations will be described and the roles played by imposed fields in affecting crystallization will be discussed. I will attempt to characterize the microscopic properties of the nonequilibrium states sampled by our systems during their phase transitions. Where possible, connections to nucleation theory and implications to crystal growth will be made.

Computational Design of Clay Minerals: Hydration of Na^+ Exchange Cation Placed on the Basal Surface of Clay Minerals

L. Gorb, J. Gu, D. Leszczynska, **J. Leszczynski**

1400 J.R. Lynch St.; Dept. of Chemistry, Jackson State University, Jackson, MS

and

Florida State University, Tallahassee, FL

A central problem in the study of clay mineral surface chemistry is understanding and correctly describing the molecular mechanisms of surface reactions. It is also well known that the proper understanding of molecular mechanisms of clay mineral surface chemistry is almost impossible without the understanding of the behavior of surface clay-water complexes. To achieving these goals, it is now generally accepted that computer simulation can contribute significantly.

In this study, we present the results of ab initio quantum-chemical investigation of hydration of Na-exchange cation placed on basal surface of clay minerals. The calculations have been performed in the framework of cluster approximation, which is extremely popular in semiempirical and ab initio calculations of zeolites. The Pople's 6–31 G(d) basis set has been chosen. Several steps for this calculations have been performed.

On the first step we have chosen the cluster consist of silica-oxygen and alumina oxygen surfaces which mimic the basal surface of clay minerals. The full optimization of this cluster has been performed and the good correspondence with the typical values of geometrical parameters of clay minerals have been shown.

To make the isomorphic substitution of the A1 atom of alumina-oxygen layer has been replaced by Mg atom. The geometry of the cluster has been reoptimized. To find the position of an exchange cation the molecular electrostatic potential has been calculated and the area of most negative electrostatic potential has been located.

Ab Initio Molecular Dynamics Study on Ag_n, with n=4,5,6

Z.F. Liu, and W.L. Yim

Department of Chemistry
The Chinese University of Hong Kong
Shatin, Hong Kong, China

and

John S. Tse

Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontario K1A 0R6, Canada

Abstract

Ab initio Molecular Dynamics (MD) method, based on density functional theory (DFT) with planewaves and pseudopotentials, was used to study the pseudorotation in silver cluster Ag_n, with n=4-6. Calculations on the neutral, cationic and anionic silver dimer Ag_2 showed that the potential surface calculated by DFT was of good quality. Simulation of Ag_4, Ag_5, and Ag_6 in canonical ensemble revealed distinct characteristics and isomerization path for each cluster. At high temperature, pseudorotation in Ag_4 was extensive, while for Ag_5 and Ag_6, the clusters maintained the planar structure, with atomic rearrangement observed for Ag_5 but not for Ag_6. At lower temperature, Ag_4 could exist in two planar structures; Ag_5 was found to be stable only in the planar form; while Ag_6 was stable in both planar trigonal and 3D pentagonal structures. In addition, micro-canonical MD simulation was performed for all three clusters to obtain vibrational density of state (DOS) plots.

PARAMAGNETICALLY INDUCED NMR RELAXATION IN SOLUTIONS CONTAINING S ≥ 1 IONS: A NEW THEORETICAL MODEL.

L. L. Lohr, R. R. Sharp, and S. M. Abernathy

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055

The enhancement of NMR relaxation rates produced by paramagnetic solutes is physically different for electron spin $S \geq 1$ species than for $S = 1/2$ species. When the zero-field (zfs) energy is larger than the electronic Zeeman energy, the electron spin precessional motion is spatially quantized with respect to the molecule-fixed principal axis system of the zfs tensor rather than along the external laboratory field direction. We have derived an analytic theory (*J. Chem. Phys.* **107**, 7620 (1997)) in which the motion of the electron spin is described in this system while that of the nuclear spin variables is described in the laboratory frame. The theory displays the dependence of the relaxation enhancement on molecular structure variables in a simple and physically transparent form. The even-electron case, illustrated by the orthorhombically distorted $Ni(II)(acac)_2(H_2O)_2$ complex with $S = 1$ and by the axially symmetric Mn(III) tetraphenylporphyrinsulfonate complex with $S = 2$, differs from the odd-electron case, for which Kramers' degeneracy obtains in zero-field. The latter is illustrated by Co(II) ion in the orthorhombically distorted $Co(II)(acac)_2(H_2O)_2$ complex with $S = 3/2$ We have calculated the energy levels, magnetic moments, and g values for the complexes using an extended crystal-field model with spin-orbit coupling, and used the results to interpret magnetic susceptibility and proton relaxation data.

Ab Initio Simulation of Physisorption: N_2 on Graphite

Gerald H. Lushington and Cary F. Chabalowski
U.S. Army Research Laboratory, AMSRL-WM-PC Aberdeen Proving Ground MD 21001-5066 USA

ABSTRACT

Potential application of activated carbon filtration systems to air decontamination and purification has led to increased interest in characterizing those microscopic factors influencing the adsorption of specific target gases onto graphitic surfaces. This paper describes a correlated ab initio supermolecular characterization of N_2 interacting with a graphitic surface model constructed as a stack of small planar aromatics. Our results are in reasonable quantitative agreement with empirically fitted parameters such as the effective adsorption diameter and sticking coefficient for N_2 interacting with the surface of a slit shaped pore. Theoretical adsorption diameters appear to vary significantly as a function of N_2 orientation, and to a lesser extent with respect to N_2 approach of different surface positions, however the overall range (3.411 - 4.053 Å) effectively encompasses the empirically determined average value of 3.493 Å. The computed sticking coefficients have a range of 0.0373 - 0.0749 eV which is on the same order or magnitude as, but consistently below, the empirically derived mean of 0.0826 eV. Some of the orientation dependencies, such as the difference between the parallel and perpendicular adsorption potentials, appear readily reproducible within the popular Steele parametrization, provided N_2 is treated as a nonspherical entity. The energetic variation observed for differing surface position can not be accomodated by Steele potentials, however, suggesting that the accuracy of classical simulations could be improved by using a nonuniform surface model. Finally, our study indicates that multi-layer effects seem to be fairly small, thus future theoretical analyses may wish to sacrifice the multi-layer nature of the surface model in favor of a larger single layer (e.g., pyrene) description.

Quantum Chemical Calculations on Ion-Molecule Processes

Robert G.A.R. Maclagan

Department of Chemistry, University of Canterbury, Christchurch New Zealand

Details of three recent calculations on ion molecule systems will be presented:

1) The reaction of SO_2^+ + H_2 which is unusual in that there is an activation barrier for an ion-molecule reaction.
2) The reaction of $C_4H_2^+$ + C_2H_2 which has been considered important in the formation of soot in flames.
3) The potential energy surface for He + CO^+ and the calculation of the gas phase ion mobility of CO^+ in He.

Transition States for 1,2 Elimination of HX (X = F, Cl) From Trifluoroethane and Chloroethane: Test Case Studies

Jaime M. Martell and Bert E. Holmes

Chemistry Department, Lyon College, Batesville, AR 72503-2317

Density functional theory and high level conventional *ab initio* calculations, together with RRKM calculations, have been employed to study the nature of transition states for 1,2 elimination of HCl from chloroethane-d_0,-d_2,-d_3,-d_5, and HF from 1,1,1-trifluoroethane-d_0,-d_3; these serve as test cases for 1,2 HX elimination from halocarbons. Quantities calculated include transition state geometries, vibrational frequencies, kinetic isotope effects, and activation energies. Of all the methods employed, the best overall performance is given by the B3PW91/cc-pVDZ method, which is computationally inexpensive compared to the high level conventional *ab initio* methods used.

Cluster model study of ZnO relaxation

João B. L. Martins[1], Elson Longo[2], Carlton A. Taft[3]

1. UNESP, Faculdade de Ciencias, Departamento de Química, Bauru, São Paulo, 17033-360, Brazil
2. Centro Brasileiro de Pesquisas Físicas - Departamento de Matéria Condensada e Física Estatística - R. Xavier Sigaud, 150, Rio de Janeiro, R.J. CEP 22290-180 - Brazil.
3. Universidade Federal de São Carlos - Departamento de Química - CP 676 - São Carlos - CEP 13560-905 - S.P. - Brazil.

The relationships between relaxation and reactivity of oxides are of great interest in the mechanistic field. The ZnO semiconductor have many experimental available data on reconstruction and reactivity. We have studied using semiempirical and ab initio methods, the effect of ZnO surfaces relaxation on H_2 and H_2O adsorption, as well as surface hydroxyl formation. We have used cluster models in order to represent the $(10\bar{1}0)$ (0001) and $(000\bar{1})$ ZnO surfaces. The density of states, Mulliken charge distribution and binding energies were studied.

Acknowledgments: FAPESP(97/13110-4 e 98/03109-1), CENAPAD-SP

A PM3 Theoretical Study of Coverage Effects for water dissociation on the MgO (001) Surfaces

A. L. Almeida[1], João B. L. Martins[2], Elson Longo[3], Carlton A. Taft[1]

1. Centro Brasileiro de Pesquisas Físicas - Departamento de Matéria Condensada e Física Estatística - R. Xavier Sigaud, 150, Rio de Janeiro, R.J. CEP 22290-180 - Brazil.
2. UNESP, Faculdade de Ciencias, Departamento de Química, Bauru, São Paulo, 17033-360, Brazil.
3. Universidade Federal de São Carlos - Departamento de Química - CP 676 - São Carlos - CEP 13560-905 - S.P. - Brazil.

We have used PM3 Semiempirical method with $(MgO)_{16}$ cluster model to study the effects of coverage upon H_2O dissociation on the (MgO) (001) surfaces. The geometry of adsorbed water molecules have been full optimized. We have analyzed the dissociation gemetries, Mulliken population, dissociation energies, and band gaps. The frequencies of hydroxyl groups are also studied. Hydrogen species diffusion takes place forming hydrogen bonding.

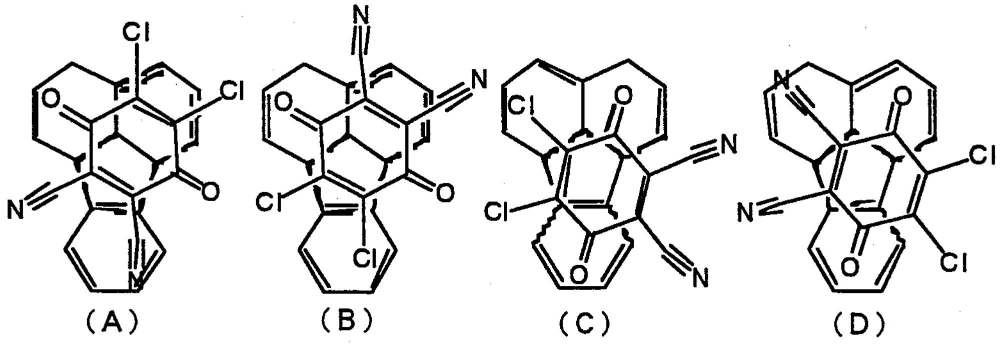
Acknowledgments: LNCC, CNPq and FAPERJ

Theoretical Study on Fluoranthene-2,3-Dichloro-5,6-Dicyano-*p*-Benzoquinone (DDQ)

Hidenori MATSUZAWA*, Kozo KOZAWA# and Tokiko UCHIDA#

*Department of Chemistry, Chiba Institute of Technology, 2-1-1 Shibazono,
Narashino 275-0023, Japan
#Department of Industrial and Engineering Chemistry, Faculty of Science and Technology,
Science University of Tokyo, Yamazaki, Noda 278-8510, Japan

Fluoranthene (FL) forms weak CT complex with DDQ molecule. Three type crystals have been found about this complex: one solvent-free crystal **(1)** and two solvent-containing [1,2-dichloroethane **(2)** and benzene **(3)**] crystals. By the X-ray structural analysis, the donor-acceptor arrangements in these crystals can be classified into four types as shown in Figure 1.



(A) (B) (C) (D)

Figure 1. Donor-acceptor arrangement patterns in the crystal structures

We report theoretical study on the geometrical and electronic structures about the two component molecules, FL cation radical, DDQ anion radical, and FL-DDQ complex pair. The stabilities of the four donor-acceptor arrangements in Figure 1 is also examined with ab initio calculation. Basis set used was 6-31G*. The calculations were performed by using the restricted or unrestricted Hartree-Fock (RHF or UHF) and density functional (B3LYP) methods with Gaussian 94 Program Package. The optimized structure of FL-DDQ complex is in good agreement with type (D). At the RHF/6-31G* level of calculation, the estimated intermolecular distance of 3.84Å is longer than that of the experimental result (3.26-3.31Å), and the stabilization energy by the complex formation is estimated 9.7 kJ/mol after the BSSE correction. The most stable arrangement is type (D) of crystal **(1)**. The differences of the complex formation energy among the four donor-acceptor arrangement patterns are small.

Ab initio-based potential energy surfaces and related properties of the ground state $RgCl_2$ complexes: the linear conformer effects.

F. Y. Naumkin* and F. R. W. McCourt†

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Abstract

$RgCl_2$ (Rg = He, Ne, Ar) potential energy surfaces have been calculated at a high *ab initio* level (coupled cluster CCSD-T theory with up to *aug-cc-pVQZ* basis sets). Corrections in terms of empirical RgCl potentials within the formalism of perturbation of the Rg–Cl interaction in the complex have led to calculated D_0 values in agreement with experiment (within the uncertainties) for $NeCl_2$ and $ArCl_2$ with no fitting. The total 2-dimensional surfaces (with the Cl–Cl distance fixed at its equilibrium value) are accurately interpolated using effective Rg–Cl potentials derived from only three radial cuts. This procedure appears to be more reliable than the traditional Legendre polynomial interpolation. The well for the linear (L) geometry is found to be slightly deeper than that for the T-shaped geometry (by a few cm^{-1}) for $HeCl_2$ and $ArCl_2$, while being equally deep or even possibly shallower for $NeCl_2$. With the zero-point vibrational energies included, the T-shaped conformer is more stable for all three systems. Rovibrational levels and microwave (MW) spectra associated with each conformer are calculated, and the observability of the spectra originating from the linear conformer is predicted to be complicated due to lower populations of the relevant levels. The influence of the L-well on the positions of the MW lines associated with the ground vibrational state of the T-shaped conformer is found to be negligible for $NeCl_2$ and $ArCl_2$, but considerable for $HeCl_2$, as a result of the height of the potential barrier separating the two wells. For excited vibrational states originating from the T-well the presence of the linear conformer affects the rovibrational probability density significantly for the heavier $RgCl_2$ complexes as well. Calculated scattering cross sections are shown to agree well with experiment for all three systems. The L-well is found to contribute considerably. In particular, for $HeCl_2$ the scattering is found to be sensitive to the position rather than to the depth of the L-well.

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*E-mail: naumkin@theochem.uwaterloo.ca

†E-mail: mccourt@theochem.uwaterloo.ca

Nonequilibrium Molecular Dynamics Simulations of Simple Dipolar Fluids

J. Liam McWhirter and Gren Patey
Department of Chemistry,
University of British Columbia, Vancouver, British Columbia, V6T 1Z1 Canada

Nonequilibrium molecular dynamics (NEMD) simulations are being used to determine the viscosity and structure of a simple dipolar fluid under shear. The pair potential is dipolar with either a Lennard-Jones or soft sphere potential. Three types of dipolar pair potentials are considered: an Ewald dipolar potential with conducting boundary conditions; an Ewald dipolar potential with vacuum boundary conditions; and a cut-off dipolar potential. In particular, we are interested in how the shear viscosity and structure vary as the equilibrium isotropic to ferroelectric nematic phase transition is approached. These studies are being used to prepare us for the NEMD simulation of electrorheological (ER) fluids: fluids consisting of polarizable particles in a nonpolarizable medium. Ultimately, we would like to determine the dependence of the shear viscosity of an ER fluid on the shape of the polarizable particles.

Ab Initio Studies of Photochemistry of Ethylene: Vibronic Spectra, Rates of Internal Conversion, and Photodissociation Rate Constants

A. M. Mebel, A. H. H. Chang, M. Hayashi, and S. H. Lin

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan 10764

Ab initio molecular orbital calculations of potential energy surfaces for the ground and excited states of C_2H_4 are used for the prediction of vibronic spectra, rates of internal conversion between different electronic states, and photodissociation rate constants of this molecule at various wavelengths. We employed for the calculations such advanced and accurate methods as CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p) for the ground state and MRCI/ANO(2+)//CASSCF/6-311(2+)G* for excited electronic states. These provided a reliable information on geometries and vibrational frequencies of the local minima and saddle points, vertical and adiabatic excitation energies of the excited electronic states for ethylene. Vibronic spectra are determined through calculations of vibrational overlap integrals and Franck-Condon factors. We derived an approach for the calculations of the vibrational overlap integrals for the general case of displaced, distorted and rotated normal coordinates. The calculated wavefunctions are used to determine matrix elements for vibronic coupling between different electronic states. The coupling elements are utilized in the calculations of intensities of forbidden transitions in vibronic spectra and for computations of the rates of internal conversion, relevant to photodissociation processes. The rate constants for each elementary step of ethylene photodissociation at 193 and 157 nm are calculated employing the RRKM theory based on the *ab initio* surfaces and used for the prediction of the product branching ratios for various photodissociation channels. According to the calculation results, UV spectra of ethylene in the region between 6 and 8.5 eV are assigned. The lifetime of π-3p, π-3s, and π-π^* singlet excited states is shown to be on the picosecond scale and they are able to rapidly convert to the vibrationally excited ground state through internal conversion or by hopping from one potential energy surface to another via their crossing seam. The reaction heats and activation energies for various dissociation channels are predicted with the accuracy within 0.1 eV. The calculated product branching ratios are in agreement with experiment; the branching ratio for 1,1-H_2 elimination is higher than that for 1,2-H_2 elimination, the atomic elimination channels are favored at increasing excitation energy compared to molecular elimination.

Time-dependent quantum mechanical calculations on $H + O_2$ for total angular momentum $J > 0$

Anthony J. H. M. Meijer and Evelyn M. Goldfield

Dept. of Chemistry, Wayne State University, Detroit MI 48202

It is well known that the endothermic reaction

$$O_2(^3\Sigma_g^-) + H(^2S) \longrightarrow OH(^2\Pi) + O(^3P)$$

is a very important reaction in combustion chemistry. Consequently, a lot of experimental and theoretical work has been done on this reaction.

From a theoretical point of view the H + O_2 reaction forms a big challenge. Not in the least, because of a deep well in the potential energy surface, corresponding to the HO_2 radical, which supports numerous bound states and gives rise to a large number of long-lived resonances. It is therefore not surprising that rigorous quantum dynamics calculations (for total angular momentum $J = 0$) have only become possible in the last five years (See, e.g., Refs. 1, 2). Recently, we published the first calculation (to our knowledge) for $J = 1$, $J = 2$, and $J = 5$.[3]

The calculations from Ref. 3 were done with the H-O_2 distance R as quantization axis. We have investigated the importance of Coriolis Coupling in our calculations by comparing them to new calculations done with the O-O axis as quantization axis. Furthermore, we compare them to calculations done in the Coupled States approximation. We will also present new calculations for $J = 10$ and compare them to our earlier results.

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The Linear Response Theory for the Polarizable Continuum Model

R. Cammi

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universitá di Parma, Viale delle Scienze, 43100 Parma, Italy

B. Mennucci

Dipartimento di Chimica e Chimica Industriale, , Universitá di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

Abstract

In this communication we present the extension of the linear response formalism to the Polarizable Continuum Model (PCM) used for the study of the solvent effect on the molecular electronic structures.

The most relevant formal aspects of the theory are discussed and numerical applications at the Random Phase Approximation (RPA-PCM) level for the calculation of excitation energies, dynamical polarizabilities and magnetic field tensors, are also presented.

PREFERENTIAL ADSORPTION SITES FOR H_2CO AND H_2O OVER V_2O_5

E.Mola , V.Ranea and J.Vicente
INIFTA, Divisón Química Teórica
Sucursal 4, Casilla de Correo 16, La Plata 1900, Argentina

P.Arnal, L.Gambaro and H.Thomas
CINDECA, UNLP, CONICET,47-257, La Plata 1900, Argentina

Uyewa Mananu
University of Kinshasa, D.R. of Congo

From the study of sintered polycrystalline samples of V_2O_5 under a CH_3OH atmosphere it has been concluded that initial adsorption and further oxidation of CH_3OH to H_2CO, different products occurs.

The presence of H_2CO and H_2O has been detected by mass spectrometry analysis (MAS) and these intermediates play a very important role in the mechanisms suggested for reaction. The temperature programmed desorption (TPD) of the system allows one to monitor the surface continuously. There is also a competition between CH_3OH and H_2O for the adsorption sites.

In order to clarify the role play by H_2CO and H_2O, we study the preferential adsorption sites for H_2CO and H_2O molecules. Because these sites are thought to influence the catalytic properties of the surface, their characterization is an important step towards understanding how the structure of the surface influences the properties of the catalyst.

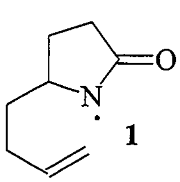
Models of the (010) plane of V_2O_5 have been utilized to find energetically favorable sites of the adsorption of H_2CO and H_2O. For this purpose, the variation of the total energy of the system was computed by ZINDO/1 type calculation.

Computational studies on π_N and Σ_N states of azolidinone and oxazolidinone radicals

Heidi M. Muchall, Nick H. Werstiuk, Benoit Daoust, and Jean Lessard

Department of Chemistry, McMaster University, Hamilton, ON, L8S 4M1, Canada

This study is based on experimental results obtained from photolysis reactions of N-chloro precursors of azolidinone radicals **1** and **2** as well as oxazolidinone radical **3**. While **1** and **3** cyclized in a 5-exo fashion, **2** did not show reactions involving the side chain. Yet the related radical **4** gave a product from an allylic hydrogen abstraction. That cyclization products were obtained as 2:1 mixtures of diastereomers raised the question of whether reactions occured from π_N or Σ_N states of the radicals. In order to get a handle on the electronic states of **1** - **3**, we have performed calculations at ROHF/4-31G, ROBecke3LYP/6-31+G(d), UHF/3-21G, and UBecke3LYP/6-31G(d) levels of theory for the model compounds **5** - **9**. The electronic ground states for the planarized species are of π_N character (A" for **5**, **7**, and **8**). Using UHF/3-21G and UBecke3LYP/6-31G(d) methods, transition states for cyclizations from π_N and Σ_N radicals were determined for radicals **1** and **3** as well as transition states for a π type cyclization and an allylic hydrogen abstraction for **2**. According to the computational results, **1** and **3** should cyclize from a π_N state. The experimentally observed behaviour of **2** and **4** together with calculations on **2** suggests that allylic hydrogen abstraction might occur in an intermolecular rather than an intramolecular manner. In addition, we have been able to locate stationary points for different conformations of **1** and **3** that show a preorientation for cyclization and indicate some form of complexation.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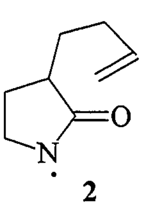
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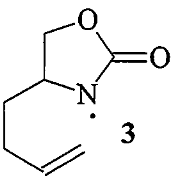
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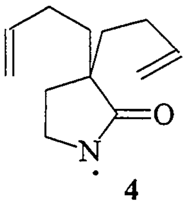
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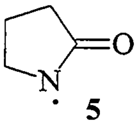
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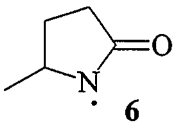
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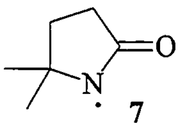
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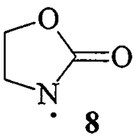
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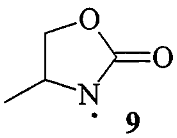
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Thermal Conductivity of Model Zeolites: Molecular Dynamics Simulation Study

Vladimir V. Murashov*

Department of Chemistry
Dalhousie University
Halifax, Nova Scotia
Canada, B3H 4J3

Thermal conductivity of model zeolites with LTA topology (characterized by a relatively simple cubic unit cell) was calculated using Non-Equilibrium Molecular Dynamics calculations. Test runs for dehydrated sodium zeolite 4A ($Na_{12}Al_{12}Si_{12}O_{48}$), a big-scale product used as an adsorbent, showed good reproducibility of the method (κ_{calc}(Na4A) = 0.6 $W \cdot m^{-1} \cdot K^{-1}$ and κ_{exp}(Na4A) = 0.65 $W \cdot m^{-1} \cdot K^{-1}$ at ambient conditions). Thermal conductivity was shown to be determined primarily by vibrations of the continuous oxygen sublattice. Hence, the most drastic suppression of heat transfer was related to alterations of the O-O distances, *e.g.* a six-fold reduction of thermal conductivity compared to siliceous LTA zeolite (κ(Si-LTA) = 1.3 $W \cdot m^{-1} \cdot K^{-1}$ at ambient conditions) was found in $AlPO_4$-LTA. Negative thermal expansion of Si-LTA in the temperature range between 100 and 300 K was related to the observed maximum at *ca.* 200 K of the temperature dependence of thermal conductivity. Counter-cations can also affect heat transfer by disturbing the oxygen sublattice locally. Resonance phonon scattering was observed for model "sodium" cations with mass more than 100 $g \cdot mol^{-1}$.

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* Present address: Department of Chemistry, University of British Columbia, Vancouver, BC, Canada

SAC-CI Study of the Photosynthetic Reaction Center of *Rhodopseudomonas viridis*

H. Nakatsuji[a,b], J. Hasegawa[a] and K. Ohkawa[a]

[a] Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

[b] Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto, 606, Japan

The excitation spectrum of the photosynthetic reaction center (PSRC) of *Rhodopseudomonas* (*Rps.*) *viridis* is successfully assigned by using the SAC-CI method. All the chromophores included in the PSRC, bacteriochlorophyll *b* dimer (special pair, P), bacteriochlorophyll *b* in L- and M-branches (B_L and B_M), bacterio-pheophytin *b* in L- and M-branches (H_L and H_M), menaquinone (MQ), ubiquinone (UQ), and four different hemes, c-552, c-554, c-556, and c-559 in c-type cytochrome subunit were calculated within the environment of proteins and waters which are dealt with by the point charge electrostatic model. The present assignment of the spectrum would give a basis for future photo-experimental studies of the PSRC. We next studied the electronic mechanism and the origin of the unidirectionality of the electron transfer from photo-excited P to H. The L-branch selectivity of the electron transfer is explained by the asymmetry of the transfer integral, an electronic factor, which originates from a small structural asymmetry of the PSRC: the L-side chromophores are locally closer than the M-side ones, though the average separations are almost the same. The smallness of charge recombination rate is attributed to the difference in electron localization between the LUMO and HOMO of P. Protein effects on the unidirectionality are quite small as far as the electrostatic model is valid, though the proteins keep the three dimensional arrangement of the chromophores in the PSRC. A mutation experiment for realizing M-side selectivity is suggested.

Gas Kinetic Theory of Sound Dispersion in Two-Component Systems

Duncan Napier and Bernie D. Shizgal
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

Recent experimental studies of sound propagation in mixtures of gases have demonstrated a new set of dispersion behaviours that are not described by conventional hydrodynamic treatments. These anomalous properties were first measured a decade ago in mixtures of gases of disparate mass(1,2). These and more recent experiments(3) have shown the existence of sound modes with propagation velocities and attenuation rates that exhibit significantly different characteristics than hydrodynamic modes. This phenomenon is attributed to the decoupling of the light and heavy components when the frequency of sound approaches the order of the collisional frequency of the gas mixture(4). Related phenomena, such as sound mode degeneracies and propagation gaps at critical frequencies and gas composition have also been studied in these systems(5).

Anomalous sound dispersion phenomena are frequently observed around the region in which hydrodynamical treatments are not valid and it is therefore necessary to use kinetic approaches. Sound dispersion relations for the system are obtained from the matrix of the linearized Boltzmann equations truncated with a modified Gross-Jackson method. The purpose of this work is to apply a gas kinetic theory of mixtures to small-amplitude oscillations near or in the Knudsen region of a gas. Experimental data suggests that oscillatory disturbances in gases exhibit complicated behaviour in this region. This work examines and interprets non-hydrodynamic behaviour observed in real systems using methods of gas kinetic theory. The method used here has been used to successfully reproduce the behaviour of simple gas mixtures and the present work is the first known application of kinetic theory to sound dispersion in mixtures gases of disparate mass.

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Symbolic Calculations of Unitary Transformations in Quantum Dynamics

Nam-Anh Nguyen and T.T. Nguyen-Dang

Département de Chimie, Faculté des Sciences et de Génie, Université LAVAL, G1K 7P4,
Québec, QC, CANADA

The present paper deals with the development of a *Mathematica* program package for handling quantum mechanical equations involving commutators and unitary transformations. We apply these new symbolic routines to test-transformations, ranging from simple translations in both spatial and momentum spaces to transformations involving non-linear generators and denoting non-inertial changes of reference frames in the phase space. We illustrate with simple examples how these tools can be used to solve formally molecular dynamical problems.

The Interplay of Spin–Orbit Coupling and Electron Correlation in Atoms and Small Molecules

Andreas Nicklass and Kirk A. Peterson

Department of Chemistry, Washington State University and
Environmental Molecular Sciences Laboratory, Pacific Northwest National
Laboratory, P.O. Box 999 MS K1-96, Richland WA 99352

Systematical series of basis sets are used at different levels of theory to determine the ground state zero-field splittings of the halogen atoms F through Br. While the convergence behavior with respect to basis set size is very similar for fully relativistic four-component calculations and a perturbational approach based on one-component wave functions, the influence of electron correlation differs significantly, thus providing new insight into the interplay of spin–orbit coupling and electron correlation.

In calculations on the spin–orbit splittings of FO, ClO, and BrO it is shown that the findings from investigating the halogen atoms also hold in molecular environments.

Finally a combination of one- and four-component calculations is applied to the electronic spectrum of the BrCl molecule.

Colouring a Lorentz Gas

Steve Nielsen and Raymond Kapral

Chemical Physics Theory Group, Department of Chemistry,
University of Toronto, 80 St. George Street, Toronto, ON M5S 3H6, Canada

A catalytic site is introduced into a two-dimensional Lorentz gas system consisting of three disks arranged in an equilateral triangle to model reactive dynamics. This system is studied at a microscopic level using an N-cylinder description where the exact dynamics is replaced by a symbolic dynamics which is a generating partition. The Kolmogorov-Sinai entropy and its finite and coloured varieties are discussed. These are then related to the coloured escape rate, a macroscopic property. Lastly, escape is eliminated by extending the three disk system to an infinite lattice, and the colour correlation function is studied. For large catalytic regions the Poisson process rate law expression breaks down.

HARDNESS PROFILE OF CONJUGATED POLYMERS

A. Neren Ökte, Yüksel İnel

Boğaziçi Üniversitesi, Kimya Bölümü
80815 Bebek/İstanbul/TÜRKİYE

The hardness, η, of a molecule is defined as half of its ionization potential and its electron affinity. There is a linear relation between hardness and bond orders. Both parameters change in the same fashion when a molecule is distorted from its equilibrium position. It has been found that hardness is also maximum at the minimum energy configuration of the molecule. Therefore, it is possible to define a hardness profile as a function of the molecular configuration.

Depending on chosen geometries the calculated band gaps of conjugated polymers are quite different. This is mainly due to the large difference in average bond alternations. It is therefore necessary to consider the effects of geometrical relaxation and electronic structure.

In this work, a series of conjugated polymers have been optimized and their hardness profiles are evaluated. Bang gap energies, E_g, were calculated and compared to experimental values available in the literature.

Electron Propagators for Large Molecules and for Highly Correlated Reference States

J.V. Ortiz

Department of Chemistry, Kansas State University, Manhattan, KS
66506–3701, U.S.A.

Several new electron propagator approximations have advantages that enable efficient, accurate calculation of correlated ionization energies, electron affinities, Dyson orbitals and total energies. For electron binding energies of large molecules, methods based on Hartree–Fock orbitals have average errors that are less than 0.2 eV, require arithmetic operations that scale with the fifth power of basis size and have symmetry–adapted, semidirect implementations with modest disk storage requirements. These techniques are illustrated by results on the photoelectron spectra of benzopyrene isomers and on electron affinities of uracyl–water complexes. For smaller molecules where nondynamical correlation is important, methods based on approximate Brueckner orbitals show considerable promise. Calculations with large basis sets on highly correlated anions and ozone produce accurate predictions of electron detachment energies. The theory that underlies these new approximations and systematic numerical characterizations of their predictive capabilities will be presented. The interpretive value of the Dyson orbitals will be shown for the benzopyrene, uracyl–water and ozone calculations.

Pressure Between Two Walls Immersed in Electrolyte Solution. Solvent Induced Effects

Frank Otto and Gren N. Patey

UBC, Dept. of Chemistry, 2036 Main Mall,
Vancouver BC, V6T 1Z1 Canada

The standard to investigate the forces between two infinite, hard walls immersed in electrolyte solution is still the primitive model (PM) which neglects all effects due to the molecular structure of the solvent. We present here a more realistic approach by using effective potentials of mean force for the ion-ion interactions (McMillan-Mayer level). Positive and negative ions have a stronger tendency to pair up due to the lack of dielectric screening at short distances. Density profiles and particle distribution functions are calculated by solving the inhomogeneous integral equations in the HNC approximation numerically.

The results for a 1:1 electrolyte between charged and uncharged walls show quantitatively and qualitatively different behaviour compared to the PM. We find long ranged attractions between like charged walls which are at least one order of magnitude greater than the corresponding dispersion interaction. For this case the PM yields only repulsive macroparticle interactions.

Stability of doubly $H_2P_2O_7^{2-}$ and triply $HP_2O_7^{3-}$ charged anion in gas phase

D. KHEFFACHE, **O. OUAMERALI**

Labratoire de Physico-Chimie Quantique, Institut de Chimie, U.S.T.H.B, BP 32, El-Alia,
Bab Ezzouar,16111, Alger-ALGERIE

Multiply Charged anions such as $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ play role of supreme importance in biochemistry. Where they appear as structural units of crystals and solutions.

The question is the following : **can these free anions exist ?**

The electronic stabilities as well as the geometry stabilities with respect to fragmentation of doubly $H_2P_2O_7^{2-}$ and triply $HP_2O_7^{3-}$ were studied theoretically at the Hartree Fock level with 6-31G* and 6-31+G* Gaussian basis sets .

The triply charged $HP_2O_7^{3-}$ anion have positive HOMO energy : 2.2eV at the corresponding optimal C_s geometry calculated at the HF/6-31+G*, indicating that this anion is electronically unstable within Koopmans' approach. It is not only the HOMO which is positive, but some others occupied orbitals are also positive. $HP_2O_7^{3-}$ has all real vibrational frequency at its optimal geometry, thus it is locally geometrically stable

Finally it is thermodynamically unstable (i.e $HP_2O_7^{3-}$ is above PO_3^- and HPO_4^{2-} dissociation fragment in the potential energy surface).

For the $H_2P_2O_7^{2-}$ dianion The orbital energy of the HOMO is negative (e= -3.4 eV at HF/6-31+G* and e= -2.8 eV at HF/6-31G*) . Which mean that this dianion is electronically stable within the Koopmans' theorem approximation.

Taking orbital relaxation into account (i.e. carrying out separate SCF level calculations on $H_2P_2O_7^{2-}$ and $H_2P_2O_7^-$) in the so-called ΔSCF treatment allows the total energy of $H_2P_2O_7^{2-}$ to be found 1.82 eV lower than that of $H_2P_2O_7^-$ at the optimal geometry

Hence the doubly charged anion $H_2P_2O_7^{2-}$ is predicted to be electronically stable at the ΔSCF level .

According to this result, we did not expect that the triply charged $HP_2O_7^{3-}$ anion could survive as metastable species in gas phase.

For $H_2P_2O_7^{2-}$ it would be good candidate to form stable dianion in gas phase and can exist as free species in solution.

Strong Field Dissociation of HCl^+ - A Comparison of Kinetic Energy Distributions

Jeff Paci and David Wardlaw

Department of Chemistry
Queen's University
Kingston, Ontario
Canada
K7L 3N6
Telephone: (613)545-6413
Fax: (613)545-6669
e-mail: jpaci@chem.queensu.ca

We are interested in investigating the properties associated with the dissociation of small molecules in strong laser fields. The split operator method has been used to solve the time-dependent Schrodinger equation for both one and two potential energy surfaces of HCl^+ subject to a strong laser field. The calculation of the kinetic energy distributions of the molecular fragments has, in the past, proved to be somewhat problematic for reasonable long laser pulse, that is, laser pulses on the order of a picosecond in length. The calculation of kinetic energy distributions requires the propagation of the dissociating wave packets for the entire duration of the laser pulse. Conventional split operator propagations require prohibitively large grids for reasonable long laser pulses. We use the fact that at large internuclear distances the Coulomb potential is approximately zero to decrease the computational effort required. A wave function splitting algorithm developed by Keller[1] for homonuclear diatomics has been extended for use on heteronuclear diatomics. We have made comparisons with the results of classical trajectory calculations on the same molecule.

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Molecular Dynamics (MD) Simulations and Energy Dispersive X-Ray Diffraction (EDXD) Studies of the Structure of Semicrystalline Poly[bis(phenoxy)phosphazene]

R. Caminiti,[a] K. B. Lipkowitz,[b] G. M. Lombardo,[c] and **G. C. Pappalardo**[*c]

(a) INFM, Dipartimento di Chimica, Università La Sapienza, p.le A. Moro 5, 00185 Roma, Italy; (b) Department of Chemistry, Indiana University-Purdue University at Indianapolis, Indianapolis, IN 46202, USA; (c) Dipartimento di Scienze Chimiche, Cattedra di Chimica Generale, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

The use of combined theoretical (MD) and X-ray (EDXD) techniques has been found recently to be successful for the determination of local structures and conformations of amorphous polymeric materials [1]. The MD simulations of models produce theoretical radial distribution functions (RDF) that are compared with the EDXD data. In the present work we studied the technologically important $[P(O\text{-}C_6H_5)_2{=}N]_n$ polymer (PBPP). Using the CHARMm potential energy function and a parameter set developed by us *ad hoc* for poly-aryloxyphosphazenes [1], MD simulations showed that the polymer occurs in the bulk as a mixture of three different phases: i) small sized (nano- and/or micro-) crystalline; ii) intermediate disordered in which the chains retain "memory" of the crystalline phase; iii) completely randomly disposed, composed of a huge number of nano- and/or micro-crystals randomly oriented to each other. Accordingly, the PBPP is a very complicated system. The EDXD RDF for such a semicrystalline material was reproduced, portion by portion, by using separate models, each of which has its own crystalline order (short interatomic distances), partial loss of memory (intermediate distances), and fully disordered phase (long distances). The results agree with X-ray diffraction experiments [2] which indicate that PBPP crystallizes with a moderate 3D crystallinity (monoclinic cell with a=13.8, b=16.6, c=4.91 Å, γ=83.0°). The MD calculations provided atomic level detail concerning the short distance ordered phase (the planar *trans-cis* (TC) conformation of the chains) as well as the relative orientation of the chains in the unit cell. In addition the analysis of the fluctuations and equilibrium geometry were attained by the theory.

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NMR chemical shifts in MNDO approximation: Parameters and results for H, C, N, and O.

S. Patchkovskii[a] and W. Thiel[b]

(a) Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4 Canada; (b) Organisch-chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

Evaluation of the NMR chemical shift tensor was implemented at the semiempirical MNDO/d level using gauge-including atomic orbitals (GIAOs) and analytical derivative theory. All relevant contributions to the chemical shifts of nuclei and points in space (NICS), including three-center terms, can be computed by the program. Execution time is dominated by the evaluation of the three-center terms, which typically require more than 90% of the total effort. Calculations with standard MNDO parameters overestimate the variation of the paramagnetic contributions, leading to a poor description of the trends in chemical shifts. Agreement with experiment is improved by reoptimizing electronic structure parameters to reproduce experimental chemical shift values for 97 small molecules and ions. One-center energies, orbital exponents and resonance β parameters on H, C, N, and O were adjusted, for a total of 16 parameters. The reference set covers chemical shift ranges of 31, 346, 933, and 1650 ppm for H, C, N, and O, respectively. Of the 290 reference shifts, 175 values refer to the gas phase. For ^1H, which is particularly sensitive to solvent effects, gas-phase data were used exclusively in the parametrization. Final RMS deviations from experiment are 0.638, 13.6, 39.6, and 80.6 ppm respectively for H, C, N, and O, down from 1.93, 36.8, 120.0, and 119.0 ppm for original MNDO. This constitutes less than 5% of the total chemical shift range for each element. A significant fraction of the total error is due to small molecules with unusual bonding. On a large set of solution NMR data for 384 common organic molecules, the RMS errors are reduced to 11.9, 38.8, and 61.7 ppm for C,N, and O, respectively. Computed chemical shifts are sensitive to the molecular geometry. Bond lengths accurate to at least 0.05Å are normally required for reasonable agreement with experiment. Three-center terms typically contribute a few ppm to the total chemical shift for all four elements studied and are essential for a qualitatively correct description of ^1H chemical shifts and NICS. These terms are less important for C, N, and O and can usually be omitted without significantly degrading the results. Notable exceptions are molecules with cumulated double bonds and systems with long-range effects due to aromatic rings. The overall quality of the results obtained with the NMR-specific parametrization is competitive with non-correlated *ab initio* calculations. Combined with a relatively low computational cost, this allows direct studies of chemical shift trends in large molecular systems. Other possible applications include rapid screening for compounds of industrial interest and direct studies of dynamical effects on shielding in extended systems.

Theoretical Study of the Interaction of Small Clusters of IrPt with H_2.

S. Castillo[1], A. Cruz[2], **J.A. Peraza**[1], and V. Bertin[3].

[1]Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas, 02200, México, D.F., México.
[2]IMP, [3]Depto. de Química, CBI, UAM-I, México.

We have studied respectively the planar interactions of the IrPt dimer and the $IrPt_2$ trimer in different electronic states with H_2, through *ab initio* calculations plus CI calculations. The goal of our study is to provide a model for understanding the hydrogen activation by bimetallic catalysts of IrPt. All the interactions here considered belong to the C2v approaches.

The IrPt($^4\Delta_{xy}$) dimer is capable of capturing and breaking to the H_2 molecule. The energy potential curve of H_2-IrPt($^4\Delta_{xy}$) interaction shows a well with a depth value of 40.3 kcal/mol. At the minimum of the well it is found that the H_2 capture distance has a value of 2.6 a.u. and the H-H distance bond has a value of 2.8 a.u.. While, the potential energy curve of IrPt($^4\Delta_{xy}$)-H_2 interaction shows a well with a depth value of 47.5 kcal/mol. In the minimum of this well, the H_2 capture distance from platium has a value of 2.9 a.u and the H-H distance bond has a value of 1.9 a.u.

We have found that the trimer of $IrPt_2$ in the state $^2A_1$ captures and breaks spontaneously H_2. For the H_2 approach to Pt2 side of $IrPt_2$ the depth of the potential energy well has a value of 78 kcal/mol. While for the H_2 approach to Ir side of $IrPt_2$ the depth of the energy potential well has a value of 40 kcal/mol.

Our results are in agreement with the activity experimentally shown by the catalysts of IrPt in presence of H_2.

Gauge Field Optimization of Classical Fluid Expansions

L Samaj and J.K. Percus

Courant Institute and Physics Department,
New York University, 251 Mercer Street, New York, NY 10012

For classical fluids with pairwise particle interactions, the Mayer diagrammatic series expansion of the grand potential in fugacity is the progenitor of numerous theoretical developments. We generalize this now traditional format by introducing a gauge degree of freedom via local vertex factors. Finite series truncations are then used variationally to determine effective gauge fields. For a test model of 3-dimensional hard spheres, the pressure resulting from optimization at the first few truncation orders is comparable with that of the Carnahan-Starling approximation. The gauge field technique is extended as well to free energy density expansions, and some preliminary results are presented.

Comparison between ethylene and propylene polymerization mechanisms with zirconocene catalysts.

L. Petitjean[(a)], D. Pattou[(a)] and M.F Ruiz-López[(b)]

[(a)] Groupement de Recherches de Lacq, Elf-Atochem, BP 34, 64170 Artix, FRANCE.
[(b)] Laboratoire de Chimie Théorique, UMR CNRS-UHP 7565, Université Henri Poincaré Nancy I, BP 239, 54506 Vandoeuvre-les-Nancy Cedex, FRANCE.

In a previous work,[1] we have described three possible mechanisms for ethylene polymerization mediated by zirconocene catalysts. This study has been done using theoretical calculations at the Density Functional Theory level with double-ξ basis sets. The active species was assumed to be the cation $[Cp_2ZrEt]^+$ (Cp=cyclopentadiene, Et=ethyl) in which a β-agostic interaction is present. Indeed, the role of agostic interactions in the reaction has been shown to be fundamental. Basically, the three proposed mechanisms depend on the initial attack orientation of the monomer and the way the chain reorients to allow for insertion. Our results confirm the existence of the so-called frontside and backside attacks, obtained by other authors [2] at a lower theory level. However, for the frontside mechanism, which is much more favorable than the backside one, we have found substantial differences. Besides, a new mechanism, referred to as stepwise-backside, has been predicted. This mechanism is indeed competitive with the frontside reaction path. In our computations, we have also shown that the attack of the monomer may proceed through a perpendicular orientation since it favours chain rotation and insertion.

In principle, the main features of the potential energy surface are expected to be similar in the case of propylene polymerization but several aspects deserve a careful analysis. For instance, it is not clear at all whether a perpendicular attack of a propylene unit to the active species is possible or not, since steric interactions change considerably with respect to the ethylene case. In addition, it is interesting to investigate which are the principal factors that may affect the stereochemistry of the reaction.

In this communication, we present some preliminary results on the reaction mechanism for propylene polymerization that are compared to calculations for ethylene. Density Functional methods are employed using gradient-corrected functionals and double-ξ basis sets. Geometry optimization is carried out for both reaction intermediates and transition structures.

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Semiempirical energy calculations on the myelin basic epitope protein MBP_{74-85} : elaboration of agonist and antagonist motifs in autoimmune disease

J.M. Pires, J.M. Matsoukas, and G.J. Moore

Department of Pharmacology & Therapeutics, Faculty of Medicine
The University of Calgary, 3330 Hospital Drive NW
Calgary, AB T2N 4N1, Canada

Conformational properties of the myelin basic protein epitope QKSQRSQDENPV (MBP_{74-85}) which can initiate experimental autoimmune encephalitis (EAE), an animal model of multiple sclerosis, were investigated by semiempirical methods. Energy calculations were carried out on the full MBP_{74-85} autoantigen and the antagonist analogue $[Ala^{81}]MBP_{74-85}$ as well as smaller semimimetic peptides. These studies have revealed a low energy cyclic conformation for MBP_{74-85} which is characterized by an agonist motif comprising an interaction of the sidechains of Arg^{78} and Asp^{81} of MBP_{74-85}. For the T cell receptor antgonist $[Ala^{81}]MBP_{74-85}$, disruption of the agonist motif by removal of the residue 81 carboxylate invokes a compenstory rearrangement of the molecule resulting in interaction of the Arg^{78} and Lys^{75} sidechains with Glu^{82}. This antagonist motif was incorporated in semimimetic peptides having the general structure Ser-Arg-LINKER-Glu-NH_2 (where LINKER = one or more residues of aminocaproic acid or isonipecotic acid) which have preferred conformations characterized by interaction of the carboxylate with both the guanidino and amino groups. In EAE assays, these small semimimetics turned out to be partial agonists, i.e. molecules with structures between agonists and antagonists. These findings provide insight into the design of small molecule (orally active) autoantigen antagonists for the treatment of autoimmune diseases such as MS.

Prediction of the Rates of Hydration of Simple Carbonyl Compounds Using the ECDE Method.

Vladimir Pitchko and J.Peter Guthrie

Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7,
Canada

Rate constants for acid, base, or un-catalyzed addition of water to carbonyl compounds can be predicted using a simple ECDE (Equilibrium Constants and Distortion Energies) method previously used for cyanohydrin formation [1] and proton transfer reactions [2]. The detailed model for hydrate formation involves at least three reaction coordinates: C-O bond formation, which would lead to a hydrate with an orthogonal geometry; conversion of the carbonyl center from sp^2 to sp^3 ; transfer of a proton from water acting as nucleophile to water or hydroxide; in the case of acid catalyzed reaction there is a fourth reaction coordinate, transfer of a proton from hydronium ion to the carbonyl oxygen. Allowance must be made for the partial desolvation of hydroxide ion if it is in contact with the carbonyl carbon. The energies of the "corner structures" can be calculated from the known energies of the reactant and product, and strain energies obtained by quantum-chemical calculations. The energy surface can be derived from these corners using a quadratic interpolation formula. The transition state energy is then determined by the lowest energy path over this energy surface.

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Absorption spectrum of chromone: A study applying and comparing the CASSCF/CASPT2 and the time-dependent density functional method

Robert Polly and Peter R. Taylor
San Diego Supercomputer Center
10100 John J. Hopkins Drive
La Jolla, CA 92093

Chromone (or benzo-γ-pyrone) and its derivatives are widely spread in plant life, mostly as pigments in plant leaves and flowers. Although the important role of these molecules in plant physiology little is known about the theoretical background of the absorption spectrum of these molecules. We performed a study of the absorption spectrum of the chromone molecule applying the CASSCF/CASPT2 method and the time-dependent density functional theory method (linear response).

The geometry of the chromone molecule in the CASSCF/CASPT2 methode has been determined by a full second-order geometry optimization using DALTON. At these geometries the vibrational frequencies of the ground state as well as the excitation energies to single-excited states have been determined. The latter has been carried out by means of a CASPT2 calculation using MOLCAS. The result show that the excitation energies are in good agreement with experimental investigations of the absorption of the chromone molecule in different solvents.

Furthermore we performed a study of the absorption spectrum employing the time dependent density functional theory. This method is suitable to describe single-excited states. The results of these calculations are is in very good agreement with experimental data and the values obtained with the CASPT2 method. Due to the capability of density functional theory to describe large molecular systems with a reasonable effort this points out that this method is a suitable method to describe the absorption of larger organic molecules.

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Simulation of solid-fluid phase equilibria for systems of chain molecules

James M. Polson and Daan Frenkel

FOM Institute for Atomic and Molecular Physics, Kruislaan 407,
1098 SJ Amsterdam, The Netherlands

We study the first order solid-fluid phase transition of a system of semi-flexible Lennard-Jones chains using computer simulation. Thermodynamic integration methods are used to calculate the free energy of the solid and fluid phases, from which a point on the melting curve is determined. The solid phase free energy per chain can be calculated to an accuracy of $\pm 0.03 k_B T$ with relative ease. The Gibbs-Duhem integration technique is used to trace out the complete melting curve, and to study the effects of chain stiffness on the transition. Increasing the chain length and stiffness both act to stabilize the solid phase. Further, we find that the density gap between solid and fluid broadens with increasing chain stiffness. The methods can be extended in a straightforward manner to study the phase behaviour of more realistically modeled chain molecules. Preliminary results for the melting transition for alkane systems are presented.

An Implementation of the COSMO Solvation Model in the Density Functional Package ADF. Part II. Refinement, Testing, and Applications

Cory C. Pye and Tom Ziegler

Department of Chemistry, The University of Calgary, Calgary, Alberta
T2N 1N4

An implementation of the Conductorlike Screening Model (COSMO) in the ADF density functional package (Version 2.3) is presented. Some new additions to our original implementation in ADF 2.0 (C. C. Pye*, Y. Han, and T. Ziegler, 3rd Canadian Computational Chemistry Conference, Edmonton, Alberta, July 19-23, 1997) are presented, including a correction for outlying charge *with gradients* and a robust iterative COSMO equation solver using the preconditioned minimum-residual biconjugate gradient method. The solvent-excluding surface is recommended over the van der Waals and original Klamt surfaces. Either the fitted or exact density may be used in calculating the C-term, with the former giving just as accurate solvation energies and using much less CPU.

Electronic and Structural Effects of Nitrogen Doping on the Ionic Conductivity of γ-Li_3PO_4

H. Rabaâ[¥] and R. Hoffmann[§]

[¥] University Ibn Tofail, Laboratoire de Chimie Théorique, PO. Box 133, 14000 Kénitra - Morocco.

[§] Cornell University, Baker Laboratory, Department of Chemistry, Ithaca, New York 14853-1301.

Abstract Electronic and structural effects on ionic conductivity in the crystalline lithium phosphorus oxynitrides γ-Li_3PO_4 and $Li_{2.88}PO_{3.73}N_{0.14}$ are analyzed, using extended Hückel tight binding (EHTB) calculations. Starting from γ-Li_3PO_4, we construct a model compound $Li_{11}P_4O_{15}N$. Our study of this model suggests that an oxygen in a bridge position (O_{II}) in the parent γ-Li_3PO_4 structure is replaced by a nitrogen to diminish the interaction between lithium ions. In addition, oxygen and lithium defects are studied. Two fundamental factors are responsible for ionic conductivity in this material; distortion of oxygen tetrahedra and the creation of defects. To study the PNP units observed in chromatographic studies, density functional calculations were also carried out on small cluster models $[(HO_3)PNP(HO)_3)]^{1+}$, $[(HO)_3POP(HO)_3]^{2+}$, $[O(P_3(OH)_3)]^{4+}$, and $[N(P_3(OH)_3)]^{3+}$. The resulting π–type orbital interaction associated with the nitrogen nonbonding orbital and the π phosphorus orbital is stronger in the P-N-P bonded compound. To produce a high mobility of lithium species in the lattice, across tetrahedral faces rather than edges, our calculations suggest that a high concentration of defects is needed.

The Theoretical Treatment of Infinitely Periodic Hydrogen-Bonded Systems

S. Raynor, M. Coté and J. Stambuli

Rutgers University
Department of Chemistry
Olson Laboratories
Newark, NJ 07102

Hydrogen-bonding can manifest itself in many different ways in a wide variety of crystalline systems. Quite subtle changes in molecular geometry can lead to substantially different types of hydrogen-bond associations between neighbors in solid-state systems. For example, although most carboxylic acid molecules form dimers in the gas phase, many crystallize in quite different forms. Some, such as formic acid and acetic acid, crystallize to form effectively infinite catemer chains, (polymer-like chains with OH-O hydrogen-bonds between monomer units), while others, such as benzoic acid, remain as dimers in the solid state. The keto-carboxylic acids provide an even more complex system. Structures involving acid-acid dimers, acid-ketone dimers, acid-acid catemers, acid-ketone catemers, and intramolecular hydrogen-bonding are all known experimentally. However, the characteristics of particular systems which lead to the formation of one type of bonding in the crystal state over another are not yet understood.

We have developed an *ab initio* approach to the treatment of infinitely periodic 3-D systems which employs the full infinite Hamiltonian operator, as well as symmetrically-identical basis set wave functions which preserve the translational symmetry of the electron density of the system. The approach can be applied at the Hartree-Fock level, or correlation can be included directly by the usual modes, since the method is wavefunction based. Because the full Hamiltonian is used, all many-body interactions are included in the calculated interaction energies, (i.e., this is *not* a pair-potential, or N-body potential, approach), and because of the translational symmetry of the basis set functions, no edge-effects occur, (i.e., this is *not* in any sense a truncated cluster approach).

On this poster, we will show the results of initial test calculations of our method. We will include some preliminary calculations performed at the *ab initio* level, as well as some recent calculations on large carboxylic acid and keto-carboxylic acid systems at the semi-empirical level.

Bottlenecks in Simulation of Free Energy Differences in Dense Fluids, and the Physics of Granular Materials

William P. Reinhardt
Department of Chemistry
University of Washington
Seattle, WA 98195-1700
USA

The problem of computer simulation of entropies and free energy differences in condensed systems has had a long and tortuous history. Thermal perturbation theory and thermodynamic integration allow, in principle, the computer to mimic reversible changes between initial and final equilibrium states, and thus computation of a free energy difference from the reversible work. In this "thermodynamic" view any reversible path connecting the two equilibrium states suffices, but concomitantly none is specified.

The difficulty is then two fold:

*although thermodynamics does not preselect a path, some paths are clearly more convenient than others: how then might an optimal one be found?

* even for what seem to be obvious path choices, convergence of such computations is notoriously slow.

The problem of path optimization may be posed in a broader context: consider the finite time, and thus irreversible, work needed to drive the system between the two states, the first being in equilibrium. The irreversible work in the two directions then bounds the desired free energy difference, and paths may be optimized, in that a better path gives tighter bounds. This works well for lattice models, but fails conspicuously for hard core fluids, in that for such systems computational convergence scales as $1/T^{-\alpha}$, for α typically in the range 1/8 to 1/4, T being a measure of computational effort. This is exceptionally poor convergence! Quite recently it has been realized that the bottleneck may be understood as an analogy to the flow and relaxation dynamics of granular materials where very slow relaxation is the norm: rapidly driven fluids behave like granular materials on time scales faster than that for hydrodynamics flow. With this realization, it has emerged that a second placing of the problem into a broader context provides a hint at a solution: Introduction and optimization of a spatially dependent metric, allows preternaturally rapid relaxation of density gradients, and for model systems speeds up free energy computations by several orders of magnitude.

Modeling Structure and Reactivity of Complex Molecular Systems

Jean-Louis Rivail

Université Henri Poincaré, Nancy I
BP 239 – F 54506 Nancy Vandoeuvre

The development of molecular mechanics and of molecular dynamics codes makes possible the simulation of molecular processes in condensed phases and in complex systems such as macromolecules. Nevertheless, chemical processes which imply breaking and making chemical bonds can hardly be represented by these oversimplified models of molecular reality and require considering the system at the level of electrons and nuclei, *i.e.* using quantum mechanics.

Combined Quantum Mechanics/Molecular Mechanics (QM/MM) treatments of complex molecular systems are becoming increasingly popular. In this talk, the principles of such an approach will be briefly outlined and illustrated by the simulation of a well-known reaction : the addition of a bromine molecule to ethylene [1].

The case of a (quasi) macroscopic molecule such as a crystal or a macromolecule is more difficult to address because the usual quantum chemical methods deal with the whole chemically bounded system, which is, in this case, far too large. For this purpose, a Local Self Consistent Field (LSCF) method [2] which allows the representation of the electronic structure of a part of the system has been developed. It works at the *ab initio*, DFT or semi empirical levels. Similarly, a Combined Classical Quantum Force Field (CQFF) has been derived [3]. It is illustrated by the study of a chemical process in an enzyme and in a tridimensional crystal (zeolite).

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Modelling Photochemistry:
Reaction Paths and "on the fly" Semi- classical Dynamics

Michael A. Robb, Stéphane Klein, Michael J. Bearpark, Barry R. Smith, Thom Vreven, Massimo Olivucci†, and Fernando Bernardi†

Department of Chemistry
King's College London
Strand London WC2R 2LS

A computational strategy for the study of the reaction paths that are relevant to organic photochemistry and photophysics is presented. This strategy involves the determination of minima, transition states and conical intersections using standard CASSCF methods[1] and "on the fly" semi-classical trajectories. The semi-classical trajectories are driven either by CASSCF gradients or by gradients from a hybrid MMVB method for large systems.

For the MMVB method, an implementation of hemi-quantal dynamics will be discussed. Here the electronic wavefunction is propagated using time-dependent quantum mechanics in synchronisation with nuclear propagation using classical mechanics so that the trajectory "feels" both potential surfaces and the non-adiabatic couplings all the time. The method should be feasible for any CI based approach although the coupled perturbed CI equations need to be solved for the real and imaginary contributions to the gradient.

The method will be illustrated with some representative computations for the radiationless decay of *all-trans* hexa-1,3,5-triene and azulene at a conical intersection channel. In the dynamics studies one observes almost pure diabatic transitions as well as situations where the trajectory propagates in a "mixed state" near the conical intersection before decay to the ground state. The results indicate that the nature and the physical interpretation of the mixed state decay depend on the topology ("peaked" or "sloped") of the conical intersection channel.

†*Dipartimento di Chimica "G. Ciamician" dell' Universitá di Bologna,*
Via Selmi 2, 40126 Bologna, Italy.

1)*Potential Energy Surface Crossings in Organic Photochemistry F. Bernardi,* M. A. Robb and M. Olivucci (Chem Soc. Reviews, 25 321-328 **1996**)

Pattern Formation in Non-Equilibrium Systems

David Ronis

Department of Chemistry, McGill University

801 Sherbrooke Ouest

Montréal, Québec, Canada H3A 2K6

Abstract

Systems far from equilibrium often fall into dynamical states that exhibit either spatial or temporal patterns, with or without defects. Simple models for two examples of these phenomena will described. In the first, a model for shark-skin texturing found on the surfaces of polymer melt extrudates will be given. In the second example, a stochastic model for light-scattering, rheology, and layering transitions in sheared colloidal suspensions will be considered.

Extension of the Centroid Molecular Dynamics formalism to include quantum statistics

Pierre-Nicholas Roy and Gregory A. Voth

Department of Chemistry and Henry Eyring Center for Theoretical
Chemistry, University of Utah, Salt Lake City, Utah, 84112 (USA)

We explore the possibility of extending the centroid molecular dynamics method (CMD) [J. Cao and G. A. Voth, J. Chem. Phys. vol. 99 p. 10070 (1993)] to the treatment of indistinguishable particles, i.e. for fermions and bosons. The CMD method has already been successfully applied to systems obeying Boltzmann statistics but the inclusion of particle interchange into the formalism remains a challenge and would allow one to address a whole new class of problems. We first consider a simple model system consisting of two non-interacting identical particles constrained to an anharmonic potential well. Both Boson (symmetric) and Fermion (antisymmetric) cases are considered, as well as the distinguishable case. The implications of the effect of quantum statistics on the centroid trajectories and on the computation of time correlation functions are discussed.

A coputational study of the reactivity of diethenylnaphthalenes towards anionic polymerization

Ahu Akın*, **Safiye Sağ Erdem***, Turgut Nugay*,
Viktorya Aviyente* and Haluk Reşat**

*Boğaziçi University, Chemistry Department, 808015, Bebek,
Istanbul, Türkiye
**Faculty of Arts and Sciences, Koç University, Istinye,
Istanbul, Türkiye

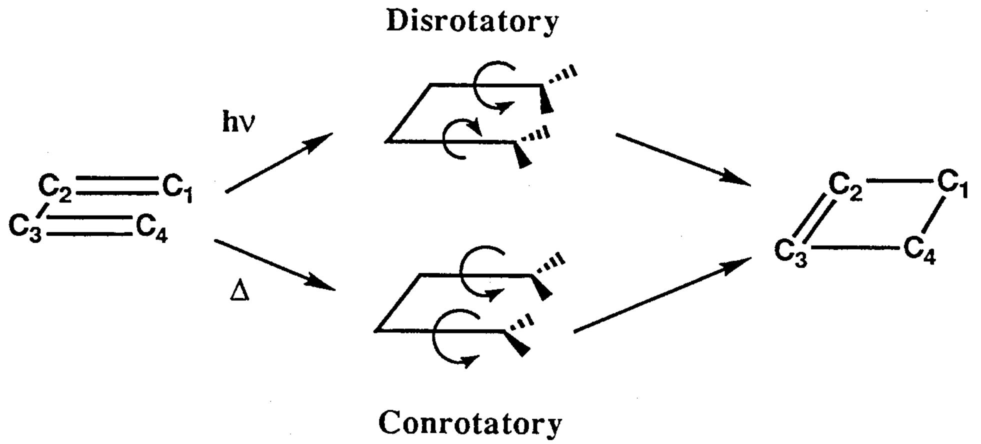
Diethenyl, di(1-methylethenyl), and di(1-phenylethenyl) naphthalenes are known to be difunctional initiators used in the synthesis of thermoplastic elastomers. Semiempirical (AM1, PM3) and *ab initio* calculations (6-31G, 6-31G*) have been carried out to determine the reactivity of these compounds towards anionic polymerization. For this purpose, geometrical parameters, electrostatic potantials, and frontier orbitals have been analyzed. Reaction paths starting from the diethenylnaphthalenes and reaching the proposed products have been studied, and transition structures along the paths have been located.

The minimum energy conformers were determined through a conformational search around single bonds for a series of disubstituted naphthalenes. We have attempted to predict how the location of the vinyl groups effects the reactivity of diethenylnaphthalenes. Our results have revealed that the most suitable difunctional initiators for anionic polymerization are the compounds where the substituents lie away from the naphthalene bridge. We have also found out that di(1-phenylethenyl)naphthalenes are more reactive than di(1-methylethenyl) and diethenylnaphthalenes.

Theoretical Studies on the Cyclic Reaction Mechanisms for s-cis Butadiene. Ground and Excited States

Shogo Sakai
Department of Information Systems Engineering
Faculty of Engineering
Osaka Sangyo University
Daito 574 Japan

It is well known that the cyclic reaction of s-cis butadiene occurs through the conrotatory path by thermal excitation and through the disrotatory path by photoexcitation.



The potential energy surfaces for cyclic reactions of s-cis butadiene at the ground and excited states were calculated by the CASSCF molecular orbital method. For the ground state, the mechanisms of both the conrotatory and disrotatory pathways were analyzed by CI-LMO-CAS method. For the excited state, two reaction paths (the avoided crossing and the conical intersection paths) were studied. The avoided crossing path produces s-cis butadiene but does not lead to cyclobutene. For the conical intersection path, the stereo selectivity (disrotatory path for the exited reaction) is controlled on the potential energy surface of the excited state. The transition state at the ground state is located in the vicinity of the conical intersection, which connects to s-cis butadiene and cyclobutene.

Performance of Density Functionals for Transition States

D.R. Salahub[1,2], S. Chrétien[1], A. Milet[1], and E. I. Proynov[1]

[1] Département de chimie, Université de Montréal, C.P. 6128 Succursale
Centre-ville, Montréal, Québec, H3C 3J7, Canada
[2]CEntre de Recherche en Calcul Appliqué CERCA 5160, boul. Décarie, bureau
400 Montréal, Québec, H3X 2H9 Canada

ABSTRACT

An overview of the performance of GGA, hybrid and LAP density functionals for transition states in a variety of benchmark systems is given. Examples, such as intramolecular proton transfer in malonaldehyde and hydrogen abstraction are considered, illustrating the difficulties which even the most advanced density functionals and post Hartree-Fock ab initio methods meet in describing some transition states.

A large class of organometallic reactions involving Pd and Fe appeared also as a very demanding task for theoretical treatment. Comparisons are reported for organometallic ligand substitutions of the type:

$$L_3PdPH_3 + CO \longrightarrow L_3PdCO + PH_3$$

and oligomerization of acetylene:

$$Fe(C_2H_2)_2^+ \longrightarrow Fe(C_4H_4)^+$$

The calculations are done with the LCGTO-KS-DFT code deMon-KS3 using a variety of different functionals. Emphasis is given to the recently developed kinetic-energy-density (τ)- dependent exchange-correlation schemes BLAP and PLAP which give superior results for most of the examples considered so far. These are compared to results of the popular GGA schemes Becke exchange-Perdew correlation (BP86) and Perdew exchange-Perdew correlation (PP86), and to results of the hybrid B3LYP method reported in the literature.

Towards Automatic Assignment of 2D and 3D NMR for Proteins

Bryan Clifford Sanctuary

Department of Chemistry McGill Univeristy, 801 Sherbrooke Street W.
Montreal, H3A 2K6

Sequence-specific resonance assignments of proteins remains the final bottleneck in the structure determination of proteins from 2D and 3D NMR. Building on previous work for the automation of the assignment process for 2D NMR, we have extended the work to include 3D NMR. There are a variety of 3D experiments designed to give spin correlations of proteins. Some give inter residue correlations, others give intra resonance information, while others give side chain resonances.

In this talk, after an introduction to 2D and 3D NMR, a description of the various algorithms will be presented. The approach first uses a partitioning algorithm to extract as many dipeptides as possible from the 3D data. At this stage the side chain information is not used. The dipeptides are then linked together as much as possible to produce back-bone polypeptides. These are matched to the protein's primary sequence. Following this, the aliphatic side chains are extracted, and mapped onto the back-bone already generated. The result is the full resonance assignment.

The programs require a good peak-picked data set, upon which the algorithms are applied sequencially. Manual intervention is allowed at all stages to help the program's efficiency and success. Results are presented on both simulated and real examples. For proteins of less than about 70 residues, the programs do as well, if not better, than manual assignments.

The main reasons for the success of the programs is the use of graph theory and fuzzy mathematics to handle the problems of missing peaks, noise and overlapped lines.

Ab initio geometry determinations of proteins

Christian Van Alsenoy,[a] Ching-Hsing Yu,[b] Anik Peeters,[a] and **Lothar Schäfer**[b]

a) Department of Chemistry, Universitaire Instelling Antwerpen, B2610 Wilrijk, Belgium
b) Department of Chemistry, University of Arkansas, Fayetteville, AR 72701 USA

We have started a program of ab initio/HF geometry determinations of proteins using the MIA approximation.[1] In the MIA procedure[1] products of two basis functions, as they occur in the SCF formalism, are expanded in terms of a set of auxiliary functions. When the MIA approximation is implemented in combination with the direct SCF approach[2], the resulting method scales linearly with system size in building the Fock matrix.

As a first example the geometry of crambin, a protein with 46 residues, was determined by ab initio HF/4-21G geometry optimization.[3] Rms deviations between calculated and crystallographic backbone structural parameters are 1.5° for N-C(α)-C' and 0.013 Å and 0.017 Å, respectively, for N-C(α) and C(α)-C'. In the case of N-C(α)-C' the rms deviations are small compared to the observed range of values, which is from <108° to >118°, confirming a definite conformational dependence of peptide backbone structural parameters on ϕ and ψ. In contrast, the deviations in bond lengths are of the same magnitude as the overall variations. The considerable non-planarity of the peptide units found in the crystal structure is well reproduced by the calculations. The phenomenon of helix compression is confirmed that is found in elongated helical chains compared to isolated residues or smaller oligomers.

Ongoing research is focused on systems whose structures are supported by water or other solvent molecules, and the general utility of ab initio geometries of large fragments of proteins in crystallographic investigations is being explored.

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Molecular Dynamics Simulations of the Sorption of Organic Compounds at the Clay Mineral/Aqueous Solution Interface

Brian J. Teppen [a], *Ching-Hsing Yu* [b], *David M. Miller* [c] *and* ***Lothar Schäfer*** [b]

[a] Advanced Analytical Center for Environmental Sciences, Savannah River Ecology Laboratory, Aiken SC 29802 USA; [b] Department of Chemistry and [c] Department of Agronomy, University of Arkansas, Fayetteville, AR 72701 USA;

We are involved in the development of a new research tool that enables molecular dynamics (MD) simulations of adsorption processes at the clay mineral/aqueous solution interface. In the recent past, we have succeeded in developing a valence force field for MD simulations of dioctahedral clays[1]. The set of parameters derived so far has enabled the successful MD modeling of the crystal structures of kaolinite, pyrophyllite, and gibbsite; and simulations of the swelling of Na- and Ca- beidellite clays by wetting at many different water contents yielded lattice d(001)-spacings within experimentally observed ranges.[1] Furthermore, full molecular dynamics simulations have been performed of the sorption of trichloroethene[2], one of the most abundant and dangerous environmental pollutants, and of methylene blue. The latter is being studied in order to test the mechanistic assumptions underlying a widely used method[3] that allows estimation of the surface areas of fully hydrated clay mineral suspensions.

Ongoing research is aimed at enhancing the existing database to derive FF parameters for a greater variety of clay minerals, including montmorillonites with octahedral Mg or Fe substitution, and MD simulations are executed regarding various topics, such as adsorbate packing and overall loading rates of chemically modified clays, and cation exchange equilibria.

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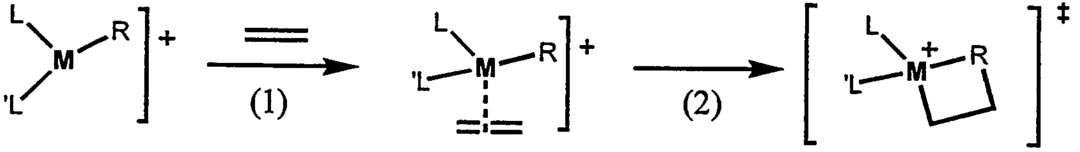
Polymerization Catalysts with d^n-Electrons ($n = 1 - 4$): A Theoretical Investigation on Model Systems.

Rochus Schmid and Tom Ziegler

University of Calgary, Dept. of Chemistry, 2500 University Drive NW
Calgary, Alberta, Canada T2N 1N4

Beginning with the early bis-cyclopentadienylsystems of group IV transition metals polymerization catalysts with a zero d-electron count are thoroughly studied both experimentally and theoretically [1,2]. Recently, it has been demonstrated that d^8-systems and even d^6- and d^7-complexes of first row elements also polymerize with good activity [3]. In an ongoing project, we investigate systems with a d-electron count from 1 to 8 by theoretical methods in order to elucidate the influence of filled d-levels on polymerization activity. This contribution presents our first results on generic complexes of the first-row transition metals with a high spin electron configuration of d^1 to d^4. A gradient corrected density functional (DFT) was used to calculate the energetics of the elementary steps of olefin coordination (1), insertion (2) and possible termination processes. We considered cationic model systems with M = Ti, V, Cr, and Mn with two auxiliary ligands (L, L' = NH_3 and NH_2^-).



Our results show that only the olefin uptake energy (1) is significantly affected by the d-electron count, which can be rationalized in terms of an analysis of frontier orbital interactions. In contrast to general belief, filled d-levels do not preclude polymerization activity for these complexes. All systems show an olefin insertion barrier well below 20 kcal/mol. Furthermore, chain termination is less favorable then propagation, which reveals that first row transition metal complexes with a d-electron count of 1 to 4 should be considered as potential olefin polymerization catalysts.

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Density Functionals From the Extended G2 Test Set

Hartmut L. Schmider and Axel D. Becke

Dept. of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

A recently developed[1] systematic procedure for the determination of exchange-correlation functionals from experimental thermochemical data was applied to the extended G2 test set of standard heats of formation by Curtiss *et al.*[2] The method was employed both in the original formulation within the GGA framework[3], and in an extended form that includes second-order corrections[4,5].

We show the impact of the inclusion of different types of data in the "training set", as well as of the truncation order of the involved series expansion. We suggest a specific reparametrization for modestly-sized basis sets, and present preliminary results along those lines.

Our residual errors in the heats of formation are presently very close to the ones obtained with G2 theory itself: 1.78 kcal/mol for the GGA fits, and 1.60 kcal/mol for the approach involving second derivatives, as compared to 1.58 kcal/mol for G2 theory.

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Uranyl Tetrahydroxide (VI), $[UO_2(OH)_4]^{2-}$. A Theoretical Study

Georg Schreckenbach, P. Jeffrey Hay, Richard L. Martin

Theoretical Chemistry T-12, MS B268
Los Alamos National Laboratory
Los Alamos, New Mexico, USA, 87545

The title compound, uranyl (VI) tetrahydroxide $[UO_2(OH)_4]^{2-}$, has been studied in detail[1] using density functional theory (DFT). Scalar relativistic effects are included approximately be replacing the uranium core with a relativistic effective core potential (ECP)[2] or by means of the quasi-relativistic method[3]. A total of nine stable structures has been characterized. Four of them possess the usual linear uranyl bond, and rapid exchange between these conformations is expected at finite temperatures. The uranyl and U-OH bond lengths of the minimum energy structure are calculated as 1.842 Å and 2.334 Å, respectively. This compares well with the experimental crystal structure values[4] of 1.824(3) Å and 2.258(3) Å, respectively. The ^{17}O NMR shielding of the uranyl oxygen in $[UO_2(OH)_4]^{2-}$ is calculated and interpreted. The existence of stable structures with a bent uranyl bond ("cis-uranyl") is predicted for the first time. Similar "cis-uranyl" structures can also be characterized for other uranyl (VI) compounds including $[UO_2Cl_4]^{2-}$ and $[UO_2F_4]^{2-}$. Such conformers are only some 10 to 30 kcal/mol higher in energy than the respective global energy minimum. Harmonic vibrational frequencies were calculated for all stable conformers of $[UO_2X_4]^{2-}$ (X = OH, Cl, F). They are compared to experiment where possible. A mechanism is suggested for the non-aqueous intramolecular oxygen ligand exchange in $[UO_2(OH)_4]^{2-}$ between uranyl and hydroxide involving a "cis-uranyl" structure as a stable intermediate in a two-step process. A similar mechanism is proposed where the solvent (H_2O) has been expliceietely included.

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A Novel Form for the Exchange-Correlation Energy Functional

Gustavo E. Scuseria

Department of Chemistry
Rice University
Houston, Texas 77005-1892
USA

A new approximate form for the exchange-correlation energy functional is developed. The form is based on the Density Matrix Expansion (DME) for the exchange functional [R. M. Koehl, G. K. Odom and G. E. Scuseria, *Mol. Phys.* **87**, 835 (1996)]. The non-local portion of the correlation energy is assumed to have the same general form as that derived for exchange, while the local portion is taken to be that of the uniform electron gas. The resulting formula does not resort to the use of exact-exchange mixing. A Kohn-Sham implementation of this functional is constructed and the parameters within the functional are adjusted to minimize the difference between the theoretical and the experimental data for a large set of atomic and molecular systems. The results are found to compare favorably with existing functionals, even those which include exact-exchange mixing.

Surface Photochemistry: When the Substrate Electrons Get Hot

Tamar Seideman

Steacie Institute, National Research Council
Ottawa, Ontario K1A 0R6, Canada

Photochemistry on metal and semiconductor surfaces has been the topic of intensive experimental and theoretical research in recent years, both due to the fascinating physics involved and due to the application to surface processing and catalysis. The observation of hot translational and internal energy distributions, anisotropic desorbate angular distributions, pronounced isotope effects and marked dependence of the product energy on the incident wavelength suggests predominance of a substrate-mediated mechanism, involving photoexcitation of surface electrons which subsequently are inelastically scattered by the adsorbate *via* a transient, electronically-excited or negative ion state. The inelastic scattering event provides a mechanism for redistributing the electron energy into the molecular degrees of freedom, which may result in a surface reaction.

New and intriguing phenomena are introduced when the substrate-adsorbate complex is excited with sub-picosecond pulses, where the field-matter interaction is typically nonperturbative. Transient, high electronic temperature generated by the photon field results in significant enhancement of the reaction yield as compared to that observed with nanosecond excitation, sensitivity of the desorbed product velocity distribution to the incident fluence and interestingly, a universal power-law fluence dependence of the yield.

Formulating a theoretical framework for understanding, and hence controlling surface photochemistry is thus an interesting challenge. The present talk outlines a newly developed quantum-mechanical theory that spans the weak-to-strong interaction range and circumvents several of the difficulties, noted in the literature, of the common approach to the problem of substrate-mediated photochemistry. Closed-form expressions for the observables show explicitly the role played by different system properties in determining the outcome, rationalizing several general observations. Photodesorption induced by short pulses involves a series of coherent transitions to and from an excited manifold, resulting in a power-law fluence dependence of the yield. Multidimensional desorption, typical of polyatomics, is dominated by an interplay between electronically excited resonances (of few femtoseconds lifetime) and vibrationally excited resonances (of picoseconds lifetimes) resulting in slow and incomplete desorption.

Strictly Correlated Electrons and the Correlation Energy of Real Systems

Michael Seidl, John. P. Perdew, and Mel Levy

Dept. of Physics and Quantum Theory Group, Tulane University, New Orleans, LA 70118

We consider hypothetic electron systems where the strength α of the electronic repulsion can be varied without changing the density distribution $\rho(\mathbf{r})$ which is for all $\alpha \geq 0$ equal to the realistic density at $\alpha = 1$. In the coupling-constant integration of density functional theory, the limit $\alpha \to \infty$ of infinitely strongly interacting electrons provides valuable information on the correlation energy of real electron systems. Using only this limit and the opposite one of weak interaction, $\alpha \to 0$, we construct a density functional for the correlation energy $E_c[\rho]$. Unlike the realistic situation at $\alpha = 1$, the strong-interaction limit $\alpha \to \infty$ seems to be simple, but in a different way than the familiar limit $\alpha \to 0$ of weak interaction. Since the electrons become strongly correlated at large $\alpha \gg 1$, we introduce the concept of *strictly correlated electrons* as a model for the extreme limit $\alpha \to \infty$. It is solved exactly for any spherical two-electron system. For the general case of more than two electrons and/or less than spherical symmetry, a useful gradient expansion is presented. We calculate accurate correlation energies for atoms and uniform electron gases.

A DFT STUDY OF SUBSTITUENT EFFECTS ON THE CONVERSION OF CARBONYL OXIDES TO DIOXIRANES

C. Selçuki, V. Aviyente

Boğaziçi Üniversitesi FEF Kimya Bölümü
80815 Bebek/İstanbul/Türkiye

The studies on carbonyl oxide chemistry have developed a lot after Criegee has proposed the well known mechanism for the ozonolysis reaction of alkenes. Although carbonyl oxides have been detected and trapped in many other reactions there is no direct evidence on their existence during the ozonolysis reactions. Dioxiranes, the cyclic isomers of carbonyl oxides have also been claimed to be one of the intermediates in the ozonolysis reactions but they have not been detected until recently. The computational studies on the conversion of carbonyl oxides to dioxiranes have lead to the conclusion that these conversions occur for carbonyl oxide and dimethyl carbonyl oxide in the gas phase although there are considerable barriers for this conversion. It has also been reported that these conversions do not take place in solution since other reactions of carbonyl oxides are favored in polar medium.

In this study, the conversion of carbonyl oxides to dioxiranes have been studied at the B3LYP/6-31G(d,p) level which has been found to reproduce the results obtained by higher levels of theory for this group of compounds. The carbonyl oxide, dioxirane and their analogs with substituents -CH_3, -CN, -OCH_3 have been fully optimized at this level and all minima have been characterized by positive vibrational frequencies whereas the transition states for the conversions have been characterized by one negative frequency. The effects of substituents have been studied in terms of their positions, electronic characters and number of substitution. In our former study, it has been shown that the solvated media changes the geometries and electronic properties of carbonyl oxides drastically. In order to observe the solvent effects on the geometries and energetics, full optimizations have been carried out in solution for all the structures where water has been taken as the solvent and has been represented by its dielectric constant (ε=78.5).

All the calculations in the gas phase and in solution have been performed by Gaussian 94 series of programs. For the solvent optimizations, the Self-Consistent Isodensity Polarized Continuum Model (SCIPCM) has been usen with an isodensity value of 0.0004au.

All Electron *ab initio* Investigations of the Electronic States of the Iron Group Carbides, FeC, CoC, and NiC

Irene Shim and Karl A. Gingerich

Department of Applied Chemistry
The Technical University of Denmark
DTU 375, DK2800 Lyngby, Denmark

The low lying electronic states of the molecules FeC, CoC, and NiC are being investigated by performing all electron *ab initio* multi-configuration self-consistent-field (CASSCF) and multi reference configuration interaction (MRCI) calculations. The relativistic corrections for the one electron Darwin contact term and the relativistic mass-velocity correction are determined in perturbation calculations. The electronic structure of the iron group carbide molecules are interpreted as antiferromagnetic couplings of the localized angular momenta of the positive ions Fe^+, Co^+, or Ni^+ with those of C^-. The chemical bond in each molecule has triple bond character in the valence bond sense. For FeC the electronic ground state is confirmed as being $^3\Delta$. The spectroscopic constants for the $^3\Delta$ ground state of FeC have been determined as $r_e = 1.585$ Å and $\omega_e = 859$ cm^{-1}. The FeC molecule has a low-lying excited state, $^1\Delta$, with $r_e = 1.567$ Å and $\omega_e = 952$ cm^{-1}. The spectroscopic data for the ground state agree well with the available experimental data. The FeC molecule is polar with charge transfer from Fe to C. The dipole moment has been determined as 1.85 D in the $^3\Delta$ ground state and as 1.51 D in the $^1\Delta$ state. The dissociation energy, D_e, is determined as 3.63 eV, and D_0 as 3.58 eV. The ground state of the NiC molecule is predicted to be $^1\Sigma^+$. The spectroscopic constants for the $^1\Sigma^+$ ground state of NiC have been determined as $r_e = 1.640$ Å and $\omega_e = 874$ cm^{-1}. Like FeC the NiC molecule is polar with charge transfer from Ni to C. The dipole moment has been determined as 2.36 D in the $^1\Sigma^+$ ground state. The work for the CoC molecule is presently in progress.

The Kinetic Theory of Planetary Exospheres and Nonthermal Escape

Bernie D. Shizgal
University of British Columbia, Department of Chemistry
2036 Main Mall, Vancouver, B.C. V6T 1Z1 Canada

One of the more challenging multidisciplinary problems in atmospheric science and kinetic theory is the study of the evolution and escape of planetary atmospheres. An atmosphere is bound incompletely to a planet by the planetary gravitational field. The exobase is the altitude for which the mean free path of atmospheric constituents is equal to the density scale height. The region above the exobase is referred to as the exosphere. For Earth, the exobase is at approximately 500 km and the exosphere is predominantly atomic oxygen, hydrogen and helium. In the vicinity of the exobase, atomic species of low mass, such as hydrogen and helium, can attain speeds in excess of the escape speed of the planet and escape, provided they suffer no further collision. The escape flux is referred to as thermal escape(1) and depends on the ambient temperature and the density at the exobase. This atmospheric escape process is analogous to a reactive process with activation energy. The velocity distribution functions of exospheric species can be very non-Maxwellian. There is an ongoing theoretical and observational effort to understand the nature of these nonequilibrium distributions. Observations generally involve measurements of Doppler profiles of hydrogen Lyman-α emission obtained from satellite instruments. Detailed reviews of this subject were published by Fahr and Shizgal(2) and Shizgal and Arkos(3).

Heavier species such as oxygen and nitrogen can escape from the atmospheres of the terrestrial planets as a result of collisional processes that are referred to as nonthermal escape mechanisms. Examples of such collisional processes are dissociative recombination, $O_2^+ + e^- \rightarrow O^* + O^*$ and charge exchange, $H^+ + H \rightarrow H^* + H$, and $D^+ + H \rightarrow D^* + H$. The asterisks denote translationally energetic particles with non-Maxwellian distributions. Dissociative recombination is believed responsible for an energetic population of oxygen atoms on Earth, Mars and Venus. Energy transfer processes, $O^* + H \rightarrow O + H^*$ and $O^* + D \rightarrow O + D^*$ are also believed to be important. This paper will provide an overview of this problem from a kinetic theory formalism based on the Boltzmann equation(3,4). Of particular interest is the differential escape rates of H and D from Mars and Venus in relation to their abundances. The observed enrichment of D relative to H is believed to be due to escape via hot oxygen impact and charge exchange and related to previous inventories of water on Mars and Venus.

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Doppler Profiles of the Distribution of O(^{1}D) Relaxing in Ne

Bernie D. Shizgal and Yutaka Matsumi
University of British Columbia, Department of Chemistry
2036 Main Mall, Vancouver, B.C. V6T 1Z1 Canada

The relaxation of hot atoms in a gaseous moderator remains a fundamental problem in rarefied gas dynamics$^{(1)}$. The rate of relaxation of energetic particles to equilibrium has important applications in diverse fields. In addition to the calculation and measurement of relaxation times, in recent years there have been numerous measurements of the details of the relaxing velocity distribution functions by Doppler spectroscopy. For example, Park et al$^{(2)}$ have investigated the relaxation of H atoms produced in laser dissociation of H_2S at 193 nm. They measured the Doppler profiles of the H atoms at the Lyman-α line during the relaxation by collisions with the rare gases and some molecular moderators. Nan and Houston$^{(3)}$ monitered the velocity relaxation of S(^{1}D) by He, Ar and Xe by measuring the Doppler profile of S(^{1}D) created by pulsed laser photolysis of OCS at 222 nm. Cline et al$^{(4)}$ reported the relaxation of hot I($^2P_{1/2}$) that was produced from photodissociation of of n-C_3F_7I at 266 nm in a background of He.

The distribution functions of O(^{1}D) in the terrestrial atmosphere can be strongly non-Maxwellian owing to the production of these atoms by photodissociation of O_2 and O_3. The relaxation dynamics of O(^{1}D) are important for a chracterization of the chemistry of the upper atmosphere. Matsumi et al$^{(5)}$ studied the velocity relaxation of O(^{1}D) produced by photodissociation of O_2 with linearly polarized F_2 laser light at 157 nm. The velocity distributions of O(^{1}D) were determined by Doppler profiles measured by VUV laser-induced fluorescence. They studied the relaxation of the energy as well as the rate of decay of the anisotropy of the distribution function. The purpose of the present paper is to study theoretically the relaxation of anisotropic distributions of O(^{1}D) in Ne with accurate quantum mechanical differential elastic scattering cross sections and to compare with both the measurements and the previous Monte-Carlo simulations that employ classical scattering cross sections. We solve the Boltzmann equation, numerically using the Quadrature Discretization Method (QDM)$^{(5)}$. A direct solution of the Boltzmann equation is obtained and the distribution function and associated Doppler profiles are determined.

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Quantum Chemical Studies of Metallo Enzymes

Per E.M. Siegbahn

Department of Physics, Stockholm University,
Box 6730, S-11385 Stockholm, Sweden.

Recent developments of quantum chemical methods, in particular of density functional methods, have made it possible to perform accurate calculations on large enough molecular systems that they are relevant in biochemistry. In this presentation examples of such calculations will be given for different enzyme systems which have been treated recently. In the first example a new mechanism is suggested for the formation of O_2 in Photosystem II. Molecular models for the different S-states will be given. In the second example the mechanisms for the different steps in Ribonucleotide Reductase (RNR) and Methane Monooxygenase (MMO) are discussed. A new mechanism for the long range communication between the tyrosyl radical and the substrate site in RNR is described.

Proton Tunneling in Polyatomic Molecules. A Direct-Dynamics Instanton Approach

Zorka Smedarchina, Antonio Fernández-Ramos, Marek Z. Zgierski, **Willem Siebrand**

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, K1A 0R6

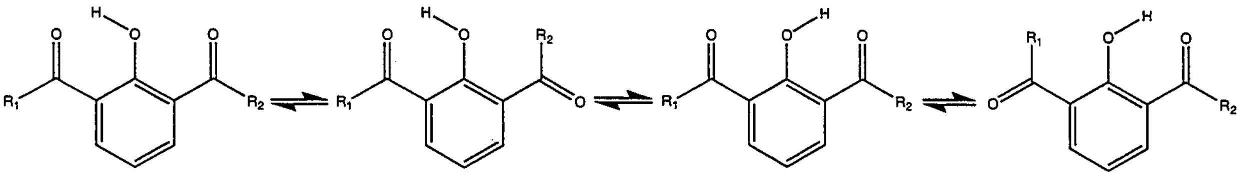
Variational Transition-State Theory (VTST) has proved to be an effective method to calculate the rates of classical over-the-barrier reactions. It is less successful, however, in dealing with quantum-mechanical through-the-barrier tunneling, the process that usually dominates proton transfer. Several versions of VTST with semiclassical tunneling corrections (VTST/ST) have been proposed and tested, but no generally satisfactory method has emerged. While classical reactions follow the minimum-energy path, tunneling reactions generally adopt a short-cut that has proved difficult to calculate for all but the smallest systems. The approximate trajectories known for the small- and large-curvature approximations are basically arbitrary and do not account properly for such qualitative features as the isotope effect. They also tend to be very laborious. To deal with these problems, the present contribution considers an alternative method based on the instanton approach. The instanton path is the dominant tunneling trajectory expressed in imaginary time. In our approach direct calculation of this trajectory is replaced by the approximate evaluation of the instanton action via a method that directly uses the input of *ab initio* quantum-chemical calculations. This action includes all the vibrational degrees of freedom of the system and governs tunneling splittings of the ground and excited levels as well as tunneling rates. A benchmark comparison of this approach with the VTST/ST approach on 9-hydroxyphenalenone, for which accurate splittings have been measured, shows that our method is far more efficient and yields superior results. The method has also been applied successfully to the rates of tautomerization of porphine and its deuterium and tritium isotopomers which span a range of 10 orders of magnitude between 100 and 350 K. To make the method generally available, a dynamics code "Dynamics of Instanton Tunneling" (DOIT) will be listed on the NRC Web site.

Hydrogen Bonding in 2,6-Disubstituted Phenols. Competitive Hydrogen Bonds and Hydrogen Bond Equilibria

Alexandra Simperler and Werner Mikenda

University of Vienna
Institute of Organic Chemistry
Währingerstraße 38
A-1090 Vienna
AUSTRIA

Intramolecular hydrogen bonding in a series of 2,6-dicarbonyl-substituted phenols has been investigated theoretically at the B3LYP/6-31G(d,p) computational level. These compounds establish an interesting model system for studying equilibria between different hydrogen-bonded conformers and in particular for evaluating the factors that govern conformational stabilities. For the unsymmetric substituted compounds there exist four basic conformers:



R_1, R_2 = H, OH, OCH_3, CH_3, NH_2

For a given compound, the stability sequence of the conformers is governed by two main factors: (i) the (attractive) hydrogen bond interaction, and (ii) the (mostly repulsive) interaction between the phenolic oxygen and the non-bonded carbonyl group. It is shown, that the stability sequences can consistently be predicted from the sum of the energies of these two contributions that have been obtained from properly chosen isodesmic reactions: (i) the hydrogen bond energy is defined by the reaction

$$C_6H_5(CO)R + C_6H_5OH \rightarrow C_6H_4(OH)(CO)R^{bonded} + C_6H_6,$$

whereas (ii) the second interaction energy is defined by the reaction

$$C_6H_5(CO)R + C_6H_5OH \rightarrow C_6H_4(OH)(CO)R^{non\text{-}bonded} + C_6H_6.$$

For all studied compounds, the stability sequence obtained in this way exactly complies with the sequence obtained from the full geometry optimization.

GAS KINETIC THEORY OF SPIN RELAXATION

R. F. Snider

Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, Canada V6T 1Z1

The dynamic behaviour of a gas at low density is governed by the Boltzmann equation. For a molecule carrying a spin, the presence of a magnetic field will cause the spin to precess, and collisions will cause the spin to reach its equilibrium state. As a consequence, a typical spin's motion is governed by a combination of precession and relaxation behaviour. This talk reviews work done over many years on different spin systems, with the objective of giving an overview of how such precession-relaxation problems are formulated and solved via use of the Boltzmann equation.

Experiment is usually aimed at observing the behaviour of a particular type of spin. Thus the simplest case is when there is only one type of spin in the system and the relaxation is governed directly by collisions, an intermolecular mechanism. In contrast, in most molecular systems, the spin of experimental interest is strongly coupled to other spins on the same molecule and relatively unaffected by direct collision processes. The relaxation mechanism is then of intramolecular type, relaxing only through the intermediary of the other spins. The observed dependence on the gas density, in particular, is very different in the two cases. Greater variety of behaviour is obtained according to whether the intramolecular coupling constants dominate the precessional motion, or vice versa. An additional complexity is attained when there is more than two spins, making it necessary to solve the precession-relaxation equations numerically. Finally, if the molecular species are chemically reacting, this also influences the precession-relaxation of a spin. Examples of each of these cases will be given.

Theoretical Studies on Boron-Lithium Clusters

Gantasala Naga Srinivas, Tracy P. Hamilton and Koop Lammertsma

Department of Chemistry, University of Alabama at Birmingham, AL 35294
Department of Chemistry, Vrije University, Amsterdam, The Netherlands

Boron-Lithium clusters are of interest as high energy additives to cryogenic hydrogen. An understanding of the bonding and energetics of these species is fundamental to the design of fuel additives. Here, we report the theoretical investigations on structure and energetics of the B_2Li_n (n = 1-6) clusters. The studies are performed at HF, MP2, B3LYP and G2MP2 level of theory using the 6-31G* basis set. As expected, the lithium atoms bridging the B_2 system are found to be global minima. Clusters with no direct B-B bond are very high in energy compared to the global minima. The B_2Li_n clusters are calculated to be thermodynamically stable towards the atomization (B_2Li_n ---> 2B + nLi). In addition, the cohesive energies (B_2Li_n ---> B_2 + Li_n) and the elimination enthalpies of Li and Li_2 units from the B_2Li_n clusters are also computed.

A Theoretical Model for the Orientation of 16-Electron CpML Insertion into the C–H Bond of Propane and Cyclopropane and Its Regio- and Stereoselectivity

Ming-Der Su

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, R.O.C.

Abstract

Complete geometry optimizations were carried out by density functional theory to study potential energy surfaces of CpM(PH_3) (M = Rh, Ir) complexes inserted into C–H bonds of propane and cyclopropane. The agreement between DFT and experimental results indicates that the B3LYP/LANL2DZ method can be a powerful tool to investigate those oxidative addition reactions. A frontier molecular orbital model suggesting the mechanistic pathway for the oxidative addition of saturated alkanes to CpML is described. It is shown that those oxidative addition reactions all proceed in a concerted fashion via a three-center transition state, and all lead to the exothermic reactions. In particular, we show that both electronic and steric effects play a major role in the preference for σ_{CH2} approach, from which one may predict the formation and stabilities of the regio- and stereoselective insertion products. Our theoretical findings suggest that highly reactive CpIr(PH_3) tends to be non-discriminating and reacts randomly while less reactive CpRh(PH_3) is highly selective. We also found that, for both CpRh(PH_3) and CpIr(PH_3) cases, the ease of oxidative addition is in the order: 2° cyclopropane > 1° propane > 2° propane. Furthermore, a configuration mixing model based on the work of Pross and Shaik is used to rationalize the computational results. It is demonstrated that both singlet-triplet energy gap of 16-electron CpML and the σ(C–H) → σ*(C–H) triplet excitation energy of hydrocarbons play a decisive role in determining reactivity as well as selectivity of CpML insertion.

Density Functional Theory Calculations of Excitation Energies of Porphyrins

Dage Sundholm

Department of Chemistry, P.O.Box 55, FIN-00014 Helsinki, Finland

Abstract

The electronic absorption spectra of pyrrole, free-base porphyrin, Mg-porphyrin, bonellin-dimethylester, and chlorophyll have been studied at density functional (DFT) level using the time-dependent DFT scheme [1] as implemented in the `TURBOMOLE` program package [2]. Complete geometry optimizations have been carried out at DFT level using the Becke-Perdew parametrization [3] and split-valence quality basis sets augmented with polarization functions (SV(P)). The basis-set study on pyrrole showed that the excitation energies of valence states are relatively insensitive to the size of the basis set, and that the excitation energies calculated using SVP basis sets are relatively close to the basis-set limit. For pyrrole and free-base porphyrin, the obtained excitation energies agree with CASPT2 and experimental results. Neither bonellin-dimethylester nor chlorophyll spectra have previously been studied at *ab initio* level.

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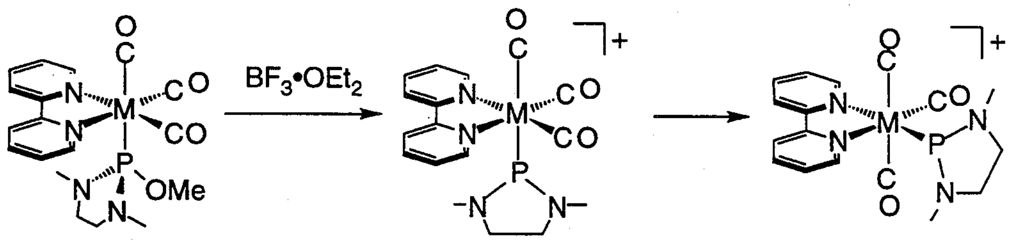
An *ab Initio* MO Study on the Isomers of Phosphenium Complexes of Group 6 Transition Metals

Keiko Takano, Hiroko Tsumura, Hiroshi Nakazawa,
Misako Kurakata, and Tsuneo Hirano

*Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka,
Bunkyo-ku, Tokyo 112-8610, Japan*

One of the authors (H.N.) developed a new preparative method of cationic phosphenium complexes for group 6 transition metals which is shown in eq 1.[1]



(eq 1)

The starting complex reacts with a Lewis acid such as BF$_3$•OEt$_2$ or BCl$_3$, an OR group on the coordinated phosphite is abstracted as an anion to give a cationic phosphenium complex with keeping its facial geometry. The complex then isomerizes to the meridional form. In this study, we investigate the influence of the geometrical isomer and the kind of group 6 transition metals in $[M(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2NMe}\}]^+$, M = Cr, Mo, W, on the nature of the M-P(phosphenium) bond by *ab initio* MO calculations.

Geometries and electronic structures of facial and meridional forms of the phosphenium complex were optimized at the Hartree Fock level of theory with the SZ and DZP basis sets and ECP. The meridional form of Mo and W complexes was found to be more stable than the facial geometry, which is consistent with the experiment. A frontier MO delocalized around the central metal and ligands was found in the *mer* isomer, which seems to contribute to the stabilization of the complex. Rotational energy barriers around M-P bond were estimated and the energy profile of the rotation were studied in the *fac* and *mer* isomers, respectively. The extent of π-back donation from the occupied d orbitals on the central metal to vacant π orbital on P atom was interpreted with geometric parameters, atomic charges, orbital populations, and so on. It will be discussed from the point of view of the isomer and the kind of metals.

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The Effect of Water on the Tautomerization of Guanine

Melissa Gee and **Fu-Ming Tao**

Department of Chemistry and Biochemistry, California State University,
Fullerton, CA 92834, USA

The keto form of guanine is converted to the enol form of guanine by the transfer of a single proton from nitrogen to oxygen. This proton transfer was studied in the presence of a water molecule, hydrogen-bonded to the guanine, and compared to the proton transfer without water. Density functional theory and ab initio methods were used with two different basis sets, 6-31G* and 6-311+G(2d,p). The theoretical calculations confirmed the keto form of guanine to be slightly more stable than the enol form of guanine with and without a water molecule. The excitation energy for the proton transfer from the keto to the enol form is 37-38 kcal/mol without water and 15-18 kcal/mol with water. These calculations show that the probability of the proton transfer would be greatly enhanced by the introduction of a water molecule.

Dynamics in Intense Laser Fields

Mark Thachuk, Duncan Napier, Robert Yanagawa, Rajdeep Gill

Department of Chemistry
2036 Main Mall
University of British Columbia
Vancouver, BC, Canada
V6T 1Z1

Recently, a semiclassical formalism for treating time-dependent Hamiltonians has been presented [M. Thachuk, M. Yu. Ivanov, D. Wardlaw, *J. Chem. Phys.* **105**, 4094 (1996); ibid, J. Chem. Phys., in press], with particular application to the dissociation of diatomic ions in intense laser fields. Two fundamental issues concerning this formalism have been discussed in depth: conservation principles and coherence. For time-dependent Hamiltonians, the conservation principle to apply during a trajectory hop depends upon the physical origin of the electronic transition, with total energy conservation and nuclear momentum conservation representing the two limiting cases. A method has been introduced that smoothly bridges the two limiting cases and applies the physically justified conservation scheme at all times. It has been shown also that the semiclassical formalism can predict erroneous results if the electronic amplitudes for well-separated hops are added coherently. This can lead to unphysical results if left unattended but methods for dealing with this issue also exist. Finally, a generalization of the well-known Landau-Zener formula to the time-dependent Hamiltonian case was derived, giving the probability of hopping at an avoided crossing as

$$P_{hop} = \exp\left[-2\pi\frac{\mathcal{V}_{12}^2(t^*)}{\hbar|d\Delta(t^*)/dt|}\right]\ , \text{ where } \frac{d}{dt}\Delta(t^*) = v\frac{\partial\Delta}{\partial R}\bigg|_{R=R^*} + \frac{\partial\Delta}{\partial t}\bigg|_{t=t^*}\ ,$$

and $v = dR/dt$ is the nuclear velocity, $R^* = R(t^*)$, and t^* is the time at which $\Delta(t^*) = 0$. The coupling and splitting between the diabatic surfaces is given by $\mathcal{V}_{12}$ and Δ, respectively. Both these quantities depend upon distance and time, in general.

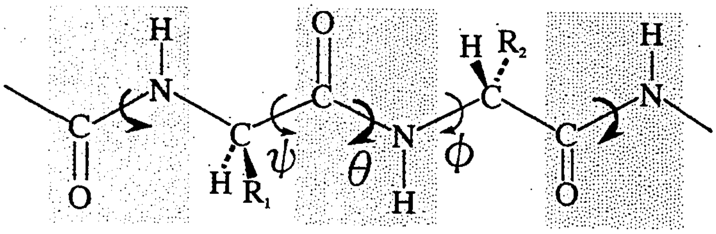
In the present work, this formalism will be used to study the dynamics of ions in intense laser fields. Using a realistic two-surface description for HCl^+, kinetic energy distributions will be analyzed. A dissociation mechanism will be presented which is intimately linked with key hops that must occur between the two surfaces. A simple model will be introduced to explain the qualitative features of these distributions.

Moving beyond diatomic ion studies to triatomic ion ones, preliminary results of the laser-induced isomerization of HCN^+ to HNC^+ will be presented. By varying the intensity and pulse duration of an intense laser, we are investigating the degree of control which can be exerted on this reaction (which does not occur under normal thermal conditions).

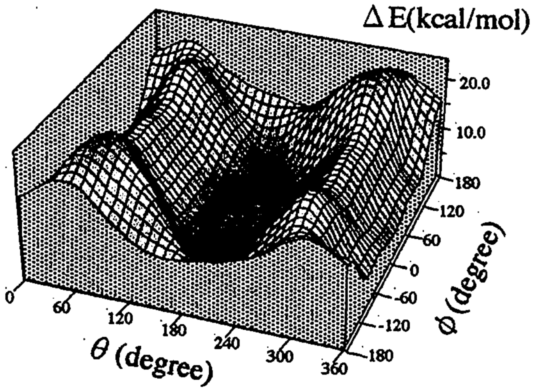
Hiroaki Tokiwa and Kei Machida

Department of Chemistry, Rikkyo University,
3-34-1 Nishi-ikebukuro, Toshima-ku , Tokyo 171, Japan

The internal rotational potential around amide bonds(peptide bonds; -CO-NH-) is an important factor for the understanding of the conformations of proteins. The high accurate rotational potential is required for molecular dynamics of proteins. However, there are only a few reports of conformational analysis using reliable *ab initio* MO method for oligopeptides even though so many theoretical and experimental studies for simple amides and amino acids have been published. We carried out conformational analysis for several neutral oligopeptides and determined the internal rotational barrier heights by using higher level *ab initio* and density functional theories. We have, furthermore, evaluated the potential energy surfaces for internal rotations because the main chain rotational angles(ψ,θ,ϕ) are closely related to each other in peptides and proteins. It is shown that the conformational dependency of oligopeptides have an important influence on intramolecular hydrogen-bonds. The conformational dependency of carbonyl-side rotation(ψ) is greater than that of the amino-side rotation(ϕ). Employing the constraint Hartree-Fock method[1] and energy-component anaysis[2], we elucidated the origin of the hydrogen-bonds which strongly affect internal rotational potentials of amide bonds.



Internal Rotaions on Oligopeptide



Potential Energy Surface with respect to Internal Rotation(θ,ϕ)

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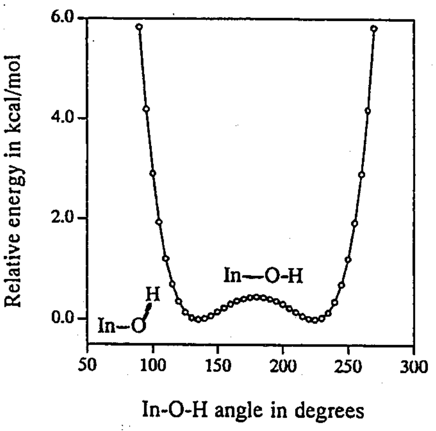
Is InOH a quasi-linear molecule?

Sundram Arulmozhiraja, Toshihiro Fujii, and **Hiroaki Tokiwa**[†]

National Institute for Environmental Studies, 16-2 Onogawa, Tukuba,
Ibaraki 305-0053, Japan, and [†]Department of Chemistry, Rikkyo University,
3-34-1 Nishi-ikebukuro, Toshima-ku , Tokyo 171, Japan

The InOH molecule has been studied experimentally, and its importance in semiconductor surface technology has been discussed briefly in recent years.[1-2] It plays a key role in the H-induced removal of In_2O_3 from the surface oxide layer of InP semiconductor substrates. The observation of InOH in the gas phase, which can be formed in a high-temperature(850°C) reaction between indium metal and water vapor, has been reported recently. The only structural report available on InOH revealed that it has a bent structure with θ(In-O-H) of 132°, however, the same authors concluded that there is a strong indication of quasi-linearity in its ground state. There is a contradictory report on its bending frequency. Since the structure and other properties of the InOH are not yet clear, and no theoretical study has yet been done, we investigated the structures and energetic nature of InOH using higher level *ab initio* and density functional theories with enough large basis set. The bent angle θ(In-O-H) and frequency number ν_2 of bending mode theoretically obtained in the present study have good agreement with corresponding recent experimental values. The bent structure of InOH molecule is more stable than the linear structure. But the energy difference between the two structures is very small, 0.22 kcal/mol at the QCISD(T) method. This finding is consistent with the very flat potential energy curve plotted as a function of θ(In-O-H). We have, therefore, concluded that the InOH molecule has a quasi-linearity. We also compared the InOH with some valence-isoelectronic molecules, such as AlOH, BOH, and so on.



Potential energy curve with respect to In-O-H angleat the MP2 level

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Fractal hybrid orbitals in iron proteins

Francisco Torrens, José Sánchez-Marín and Ignacio Nebot-Gil

Departament de Química Física, Facultat de Química, Universitat de València, Dr. Moliner 50, E-46100-Burjassot (València), Spain

A geometric model is presented to interpret the anomalous T^{3+2m} temperature dependence of the Raman spin-lattice relaxation rates in heme and iron-sulfur proteins. Analysis of relaxation data is based on a modified Debye relationship between the spectral exponent m and the density of vibrational states $\rho(v) \propto v^{m-1}$, where $0 \leq v \leq v_{max}$. Magnetic relaxation measurements on cytochrome C551 and putidaredoxin yield noninteger values of m that are influenced by changes in the ionic medium. The apparent physical significance of m is revealed, in part, by correlation to a protein's fractal geometry, which characterizes a repeating structural motif by a single parameter called the *fractal dimension* D. Estimates of D for 70 proteins are computed by a method that identifies geometric and statistical self-similarities of α-carbon coordinates; values range within the limits $(1 \leq D \leq 2)$ of well-defined test structures and correlate principally with dominant elements of secondary structures. In six iron proteins, the highest values of m derived from relaxation data are approximated by the estimated values of D calculated from the covalent structure. The fractal dimension of the tertiary structures of some iron proteins have been analyzed and compared with a Gaussian chain $D = 1.5$. The interpretation is given in terms of *steric* repulsion $(D < 1.5)$ and attractive forces between residues $(D > 1.5)$. The structure and shape of the polypeptide chain of iron proteins are determined by the hybridized states of atomic orbitals in the molecular chain. The calculated s ratio in the sp^n hybrid orbitals is computed from the fractal dimension. Two classes of iron proteins are distinguished quantitatively between each other with this representation: 1) For ferric hemeproteins, a mean value of D about 1.48 predicts a s ratio of 0.22 and $sp^{3.63}$ hybrid orbitals, beyond tetrahedral sp^3 hybrids. 2) For iron-sulphur proteins ($Fe_2S_2{}^*Cys_4$), a mean value of D about 1.26 gives an s ratio of 0.33 and $sp^{1.99}$ hybrid orbitals, very near to planar sp^2 orbitals.

The structural principles of some binary intermetallic alloys

John S. Tse, R. Rousseau and G. Frapper

Theory and Computation Program
Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontaio K1A 0R6

The electronic structure of recently discovered novel K-Ag alloys obtained from high-pressure synthesis is investigated with First Principles band structure calculations. From the topological analysis of the charge density, it is shown that the major contribution to the stability is through electron transfer from electropositive K atoms to the Ag atoms. This bonding scheme is analogus to that found in Zintl phase compounds. Therefore, the electropositive atoms can be considered as simply electron donors and the structure of the solid can be elucidated from basic electron counting rules that determine the framework of the electronegative atoms. This simple concept can be extended to other systems such as Li-Al and Li-Sn alloys. In the case of Li-Al alloys, the donation of the electrons from the Li atoms to the Al atoms strengthens the Al-Al bonds at low Li doping (e.g. $LiAl_3$ and LiAl). More localized and predominantly 2-D structures are favoured at higher Li concentrations (e.g. Li_3Al_2). A similar explanation can be used to describe the structural trends observed in the Li-Sn alloy system.

Quantum Boltzmann Equations and Muonium Interactions with Gases

Ralph Eric Turner

Department of Physics, Northwest Community College,
5331 McConnell Ave., Terrace, B.C., Canada V8G 4C2

Experimental data on the study of the interactions of muonium with various gases are available. This study uses the muon's spin to investigate the physical and chemical processes which may occur. It may be categorized by the nature of the interactions between muonium and the gas. The types of intermolecular processes that occur, such as angular momentum reorientations, spin exchanges and chemical reactions, lead to a rich precession-relaxation dynamics for the muon's spin. From a theoretical point of view, the categorization may be based on the complexity of the mathematics required to describe the dynamics of the muon's spin angular momentum during the time of data collection. In terms of the intermolecular collisional processes occuring it is as follows: (i) Chemical reactions producing stable diamagnetic molecules, (ii) Spin exchange relaxation with paramagnetic gases, (iii) Angular momentum reorientation of stable radicals, (iv) Chemical reactions involving diamagnetic gases producing radicals which undergo angular momentum reorientation, (v) Angular momentum reorientation and spin exchange of stable radicals, and (vi) Chemical reactions involving paramagnetic gases producing radicals which undergo angular momentum reorientation and spin exchange. The theoretical problem involves free (between collisions) spin dynamics coupled by the collisional processes. Solutions of the resulting quantum Boltzmann equations result in signals where the observable frequencies, relaxation rates, amplitudes and phases are, in general, dependent both upon the internal state properties of the radicals, as well as on the reorientation, spin exchange and chemical reaction collision cross sections. These are in turn dependent on the pressure and magnetic field strength.

First-principles LAPW-MD calculations on small transition metal clusters.

K. Uehara and J.S. Tse

Theory and Computational Program
Steacie Institute for Molecular Sciences
National Research Council of Cananda
Ottawa, Ontario K1A 0R6

A new ab initio molecular dynamics method (AIMD) based on the full potential linearized-augmented-plane-wave(LAPW) basis set have been implemented recently. The LAPW basis set is well suited for systems containing localized electrons such as first row atoms and transition metals. In our implementation of the LAPW-MD scheme, iterative residual minimization algorithm is used to solve the electronic states problem and SCF convergence is improved by a second-order damped dynamics method. The atoms are moved according to forces derived from the Hellman-Feynman theorem. The performance of the program is further enhanced by parallelization. We will discuss the technical details of the program implementation and present the results obtained from this code to the equilibrium structures, vibrational properties and the topological analysis of the charge densities of small transition metal clusters.

Electronic Structure of Transition Metal Complexes with Low-Coordinated Phosphorus Ligands

Steven Creve, Kristine Pierloot, Minh Tho Nguyen and **Luc G. Vanquickenborne**

Department of Chemistry, University of Leuven,Celestijnenlaan 200F, B-3001 Heverlee, Belgium

The geometries, stabilities and electronic structure of carbonyl metal complexes with typical low-coordinated phosphorus ligands will be discussed. The complexes include phosphinidenes (R-P) which are known as important transient species in phosphorus chemistry and can be stabilized through complexation with transition metal fragments. In spite of the considerable amount of experimental data available, two questions concerning phosphinidene-transition metal complexes still remain unresolved. The first one addresses the nature of the ground state spin multiplicity. In contrast to free phosphinidenes that are known to have a triplet ground state, the transition metal complexes have been proposed to be characterized by a singlet ground state. The second point concerns the amount of π-backbonding in representative complexes as $M(CO)_5$-PR, with M = Cr, Mo, W.

In order to gain some insight in these intriguing problems, ab initio MO and DFT calculations have been performed on a series of $Cr(CO)_5$-PR complexes (R = H, CH_3, NH_2, OH, SiH_3, PH_2, SH). The parent species ($Cr(CO)_5$-PH) has been studied extensively by several ab initio methods (HF, MP2, CASSCF, CASPT2) including relativistic corrections) and the B3LYP-DFT method, with the purpose of finding suitable computational methods. For the other compounds of the series, only the most reliable methods were used, which turned out to be B3LYP-DFT and CASPT2.

The formation of the Cr-P bond essentially arises from a ligand → metal σ charge transfer. While a significant amount of π back-donation is also observed for $Cr(CO)_5$-PH, $Cr(CO)_5$-PCH_3 and $Cr(CO)_5$-$PSiH_3$, this effect decreases for $Cr(CO)_5$-POH, $Cr(CO)_5$-PSH and Cr(CO)5-PNH_2, and almost no π backbonding is observed for $Cr(CO)_5$-PPH_2. Both in their lowest lying singlet and triplet states, the complexes exhibit staggered conformations. The singlet state is the ground state throughout the whole series. The observed trends are understood in terms of electronic effects.

While HF and MP2, either in restricted or unrestricted formulation, as well as CASSCF(2/2) and CASPT2(2/2) even fail to predict a correct qualitative picture, B3LYP-DFT yields reasonable qualitative and quantitative results as compared to CASPT2 (12/12).

We also consider the role of the metal fragments in the cyclodimerization of phosphaacetylene (R-C≡P). The competition between both head-to-head and head-to-tail mechanisms, with and without the presence of a metal fragment as well as the nature of the interaction will be discussed in some detail.

UNIMOLECULAR [2+2+2] CYCLOADDITION REACTION FOR [3.3.3] UNDECA-2,7,9-TRIENE

Tereza Varnalı

Boğaziçi University F.E.F. Kimya, Bebek 80815 Istanbul, Turkey.

The [3.3.3]undeca-2,7,9-triene molecule has been modeled to undergo unimolecular [2+2+2] cycloaddition reaction. The reactant product and and the transition state are studied quantum mechanically. The calculations have been carried out using G94 at 6-31G** level of sophistication. The HOMO and LUMO are illustrated. The double bonds constrained by the framework in which they are embedded allow an all antara path in which an antibonding orbital of one of the double bonds is occupied.

Quantum Dynamical Simulations of Proton Transport in Condensed Phases

Gregory A. Voth

Department of Chemistry and Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, Utah, 84112

A general theoretical discussion of proton translocation in water and biophysical systems will be given. The modeling of the interactions which mediate the translocation process will be described, including empirical valence bond treatments and *ab initio* molecular dynamics methods. The application of centroid molecular dynamics to include the nuclear quantum effects will also be outlined. In all cases, the microscopic features which affect the quantum dynamical proton translocation process will be elaborated.

Contribution of Unoccupied Cu sp States to Chemical Vibrational Frequency Shifts of CO on Cu(111)

R. L. C. Wang and H. J. Kreuzer

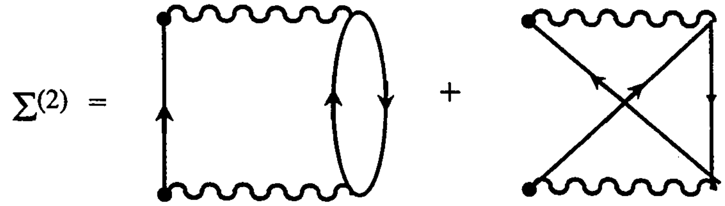
Dept. of Physica, Dalhousie University, Halifax, NS B3H 3J5, Canada

We report the calculations of the vibrational frequencies of CO chemisorbed on the Cu(111) surface based on the density functional theory. The calculated vibrational frequencies as functions of the coverage and the isotopic mixture composition are in excellent agreement with the experiments. The analyses of local density of states indecate that the unoccupied Cu sp states make an important contribution to the electron charge back donation from the Cu(111) surface to the CO's 2π orbitals and, therefore, the chemical bond. With increasing the CO coverage, the interaction of the unoccupied Cu sp states with the CO's 2π orbitals gets stronger, which pushes the latter lower, leads to more electron charge back donation, looses the C-O bond and results in a negative chemical shift of the CO stretching vibrational frequency.

Many-body perturbation techniques in the Kohn-Sham Density-Functional-Theory .

M.Waroquier, D.Van Neck, K.Peirs and V.Van Speybroeck
Laboratory for Theoretical Physics, Department Subatomic and Radiation Physics
University of Gent, Proeftuinstraat, 86, 9000 GENT, BELGIUM

The Kohn-Sham concept with the introduction of an exchange-correlation functional $E_{xc}[\rho]$ in the non-interactive scheme, is outlined in terms of one-particle-Green's functions. It is shown that any self-consistent perturbation scheme that is able to calculate the exchange-correlation functional destroys the specific advantages of the KS concept.In this work we try to construct a Kohn-Sham single-particle Green's function from a self-consistent solution of the Dyson equation for one-body Green's functions up to a specific order in the interaction. Starting from the full hamiltonian for an ensemble of interacting electrons : $\hat{H} = \hat{T} + \hat{V}_0 + \hat{V}_{ee}$ with the external one-body potential $\hat{V}_0$ representing the interaction with the atomic nuclei, the exact solution is given by the Dyson equation : $\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)\,\hat{\Sigma}(E)\,\hat{G}(E)$ in terms of the s.p. Green's function propagators in energy space [1]. $\hat{\Sigma}(E)$ contains all order "dressed" skeletons (irreducible self-energy diagrams in which all internal lines stand for exact propagators). First order self-energy diagrams lead to the Hartree-Fock solution. An insertion of second order skeletons leads to an energy dependence of the self-energy and accounts for correlations present in the many-electron interacting system. A method is given [1,2] to solve the Dyson equation up to second order. Introducing now the KS concept, we construct the KS hamiltonian $\hat{H}_{KS} = \hat{T} + \hat{V}_{KS}$ ($\hat{V}_{KS} = \hat{V}_0 + \hat{J} + \hat{V}_{xc}$) belonging to a non-interacting system yielding the same groundstate density as the one of the full interacting system. The Dyson equation defining the KS propagator is given by : $\hat{G}_{KS}(E) = \hat{G}_0(E) + \hat{G}_0(E)\,\hat{V}_{KS}\,\hat{G}_{KS}(E)$.



We present a method for the construction of the exchange-correlation potential $V_{xc}[\rho]$ defining the one-body KS potential corresponding to the self-consistent solution of the Dyson equation. This construction is unique. It is stressed that the Green's functions of both systems are different and that they lead to different g.s. energies.

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Simulations of Chemical Processes in Solutions and Proteins by ab initio and related approaches

Arieh Warshel

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1062

Several strategies for *ab initio* quantum mechanical calculations of chemical processes in solution and proteins are considered and described. This includes (i) a hybrid QM/MM approach that uses the EVB potential surface as a mapping potential for the purpose of obtaining activation free energies [1], (ii) The constraint DFT(CDFT) and frozen DFT(FDFT) methods that consider the entire solvent (or protein) quantum mechanically [2] and a hybrid *ab initio/Langevin* Dipole model [3]. The performance of these approaches is discussed and their implementation in calculations of free energies of enzymatic reactions is considered. Convergence issues and other problems are discussed and analyzed. Finally, the prospect of using such approaches in reliable studies of enzymes is compared to what can be done presently with the EVB method [4].

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The Effects of Radiation on DNA Studied by Density Functional Theory

S. D. Wetmore[a], R. J. Boyd[a] and L. A. Eriksson[b]

[a]*Department of Chemistry, Dalhousie University, Halifax, B3H 4J3 Nova Scotia, Canada*
[b]*Department of Physics, Stockholm University, Box 6730, S-113 85 Stockholm, Sweden*

Much of the recent literature has been devoted to understanding the effects of radiation on DNA. Interest in this area has arisen due to the use of radiation in cancer treatment, as well as, the speculations of radiation risks in space flight. The primary radiation effects involve base and sugar radicals which subsequently lead to DNA-protein cross-links and strand breaks. Since the spectra of full DNA are very complicated, experimental investigations have evolved around studies on the single-crystals of various derivatives of the individual DNA bases. The key experimental techniques implemented include electron spin resonance (ESR) and, the more sophisticated, electron nuclear double resonance (ENDOR). ENDOR is an important tool since it allows for the precise determination of the protonation state of the radicals generated during radiation.

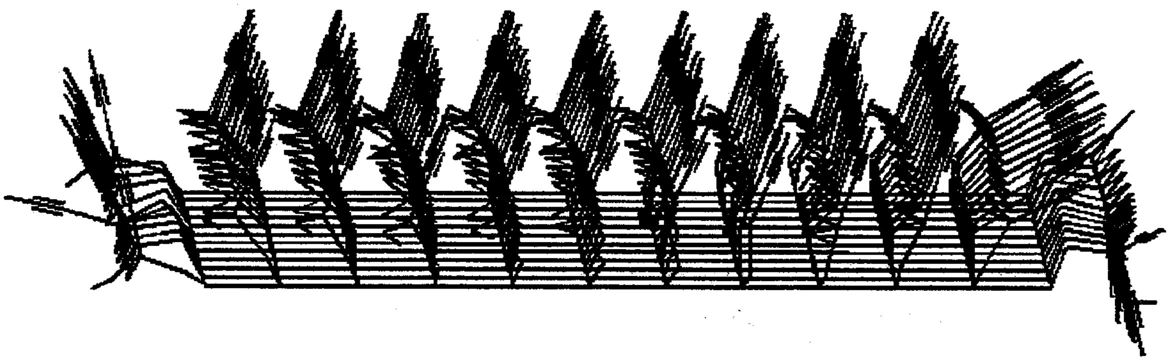
However, even the spectra obtained from ENDOR studies on single-crystal model systems are very complex due to varying degrees of hydrogen bonding and the similarity between the spectra of the radicals formed. Thus, this poster presents the calculation of the hyperfine coupling constants (HFCCs) in a wide range of DNA base and sugar radicals through the use of density functional theory (DFT). DFT is an appropriate method for biological molecules since it yields reliable HFCCs at a feasible computational cost. Comparison of experimental and theoretical HFCCs allows one to conclude which radicals have been generated during the radiation of the DNA bases.

TIN ALKYNYL BONDING TO SURFACES: CO-POLYMERISATION AND QUANTUM CALCULATIONS.

Adam Dickie and **M.A.Whitehead**
Quantum Chemistry Laboratory, McGill University,
801,Sherbrooke Street West, Montreal, Quebec, H3A-2K6.

Molecular Modelling calculations linked to PM3 calculations allow the analysis of the co-polymerisation of tin alkynls adsorbed on several model silica surfaces. The essential role of the surface in setting the conformation necessary for co-polymerisation is considered, new surface matrices are designed, and the geometry, eigenvalues and energies analysed.

The surface used is a model 12 by 12 matrix, adsorbing 144 tin alkynyls and generating 12 parallel conducting delocalised polymeric linkages.



A monolayer of $O_3Sn\text{-}C{\equiv}C\text{-}H$ on a model 12x12 Si substrate calculated by molecular modelling

A Jastrow Corrected Time-Dependent Self-Consistent Field Approximation

Joshua Wilkie[1], M.A. Ratner, and R.B. Gerber

[1]Department of Chemistry, Northwestern University,
2145 N. Sheridan Road, Evanston, IL 60208-3113

An improved approximation to the time-dependent Schrödinger equation is developed by correcting the usual time-dependent self-consistent field ansatz using a Jastrow prefactor defined via a set of variationally determined time-dependent parameters and a linearly independent set of prespecified spatial functions. The method is applicable in any number of dimensions, and computational costs scale algebraically with the number of degrees of freedom. The new formalism is applied to a two-dimensional double well potential to demonstrate the improved accuracy of the method.

A comparative PAW *ab initio* molecular dynamics study of proton transfer in 5,8-dihydroxynaphthoquinone and the formic acid dimer

Katharina Wolf, Alexandra Simperler and Werner Mikenda

University of Vienna
Institute of Organic Chemistry
Währingerstraße 38
A-1090 Wien
AUSTRIA

A Projector Augmented Wave (**PAW**) [1] molecular dynamics study of proton transfer in 5,8-Dihydroxynaphthoquinone (DHN) and the formic acid dimer (FAD) is presented. PAW is based on the *ab initio* molecular dynamics approach of R. Car and M. Parrinello [2], which carries out classical dynamics on an *ab initio* quantum mechanical potential energy surface calculated directly from first principle using accurate density functional theory.

Molecular dynamics runs with a time-interval of 0.12 fs were performed for evolution time periods of up to 20 ps. At elevated temperatures the **intramolecular** proton transfer in DHN and the **intermolecular** transfer in FAD take place at largely differing geometric situations. Short O...O distances are highly favorable for proton transfer to occur, but they are neither the sufficient, nor a necessary criterion.

The energetics of the proton motion has been modeled by calculating potential energies along a properly chosen reaction coordinate for single time steps within a "heavy-light-heavy" approximation. The proton is moving on a potential energy surface that is determined by the geometry just given. Two different kinds of transitions can be distinguished: (1) "isolated proton transfers", which start and end with strongly asymmetric single-minimum potentials, but pass through (near-) symmetric double-minimum potentials; (2) "proton shuttling periods", which include several consecutive transitions, so that we are not really dealing with proton transfer, but with a stationary proton motion within a symmetric single-minimum potential, which remains approximately constant for a longer time.

For both molecules "isolated" transfers as well as "shuttling" periods are observed which appear either as single transitions on one side of the molecule only, or as double transitions on both sides. In the case of FAD these double transitions are more likely to occur simultaneously, whereas in DHN some thousand time steps may lie in between the two events.

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Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling.

S. K. Wolff and T. Ziegler

Department of Chemistry, University of Calgary, Calgary,
Alberta, Canada, T2N 1N4

A formulation for the calculation of nuclear magnetic resonance (NMR) shielding tensors, based on density functional theory (DFT), is presented. Scalar-relativistic and spin-orbit coupling effects are taken into account, and a Fermi-contact term is included in the NMR shielding tensor expression. Gauge-including atomic orbitals (GIAO) and a frozen-core approximation are used. This formulation has been implemented, and ^{1}H and ^{13}C NMR shifts of hydrogen and methyl halides have been calculated and show good agreement with experiment. ^{13}C NMR shifts of $5d$ transition metal carbonyls have been calculated and show improved agreement with experiment over previous scalar-relativistic calculations. For the metal carbonyls, it is shown explicitly that the combination of spin-orbit coupling and magnetic field mixes spin triplet states into the ground state inducing a spin density that then interacts with the nuclei of the metal carbonyl via the Fermi-contact term. Results indicate that the Fermi-contact contribution to the ^{13}C NMR of the metal carbonyl ions increases with increasing oxidation state of the ion. It is reasoned that as the oxidation state increases, π-back bonding decreases and σ-bonding increases, within the metal-carbon bond, thus facilitating a greater transfer of spin density from the metal to the carbon nucleus, and thus increasing the Fermi-contact contribution to the NMR shielding of the carbon.

Accurate Thermochemistry for Large Molecules using a Density Functional/Locally Dense Basis Set Approach

G. A. DiLabio and **J. S. Wright**

Ottawa-Carleton Chemistry Institute and Department of Chemistry,
Carleton University, 1125 Colonel By Dr., Ottawa, Canada K1S 5B6

Bond dissociation energies (BDE's), electron affinities (EA's) and proton affinities (PA's) are calculated for a variety of molecules containing C-H, N-H, O-H and S-H bonds using density functional theory with the B3LYP functional. Thermochemistry in which these bonds are broken or ions are formed are particularly relevant to understanding proton transfer (acid-base), electron transfer (redox) and free radical reactions in biochemical systems. A series of basis set experiments led to choice of the 6-311+G(2d,2p) basis as the optimum compromise between computational speed and thermochemical accuracy. Two important modifications to the standard DFT approach were necessary, however, to make the accuracy approach 1 kcal/mol. This included use of an ROB3LYP calculation for radicals, as opposed to the normal (UHF)B3LYP calculation, as well as a correction for the hydrogen atom self-interaction energy to avoid the excessively low energy obtained with the standard approach. With these modifications a series of "protocols" were developed which fully define the DFT calculation, including determination of geometry, frequency, enthalpy corrections and single-point energies. These protocols allow choice of an appropriate theoretical procedure according to molecular size, while maintaining a known level of accuracy. In general, the medium and higher-level protocols do approach the target accuracy of 1 kcal/mol for a variety of molecules containing the X-H bonds given above, although the results are somewhat inferior for BDE's between two heavy atoms. Application of the above methodology to determine gas-phase acid dissociation constants gave excellent results when compared to experimental values.

Using this basic framework, the approach was modified to allow treatment of much larger molecules. The method combines the use of locally dense basis sets (LDBS) with density functional theory including the features described above. For water, propene and the water dimer, primary bonding regions were treated with a large basis while more distant regions were described by progressively smaller basis sets. For the calculation of the BDE for water, for example, corresponding to $H_2O \rightarrow OH + H$, we defined the primary region to be the O-H bond to be broken, and the secondary region to be the other H atom. We then studied the BDE as a function of secondary basis, using a large primary basis. The fortunate result is that the BDE is very insensitive to the nature of the secondary basis, giving a range of only 0.3 kcal/mol for the entire range of secondary basis sets (from STO-3G on up to the full basis). Finally, we applied the DFT/LDBS method to the determination of the BDE for the phenolic O-H bond in α-tocopherol (Vitamin E), a molecule of biochemical importance containing 81 atoms. Four separate regions were defined, where the O-H bond was primary, the benzene carbon atoms secondary, and the 16-carbon phytyl tail quaternary. The results agreed closely with the full basis calculation for a Vitamin E model compound. The above methodology can be implemented using standard quantum chemistry packages without modification, e.g. Gaussian-94.

PARTICIPANT LIST

Dr. Misako Aida
National Cancer Centre Research Institute
Biophysics Division
5-1-1 Tsukiji, Chuo-Ku
Tokyo, 104-0045
Japan
tel: 81 3 3542-2511
fax: 81 3 3546-1369
maida@ncc.go.jp

Dr. Fumhiko Aiga
Materials & Devices Research Laboratories
1, Komukai Toshiba-cho
Saiwai-ku
Kawasaki, Kanagawa 210-8582
Japan
tel: 81 44 549-2131
fax: 81 44 520-1286
fumihiko-aiga@mdl.rdc.toshiba.co.jp

Mr. Saman Alavi
University of British Columbia
Department of Chemistry
2036 Mail Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6549
fax: 1 604 822-2847
alavi@theory.chem.ubc.ca

Ms. Julianna A. Altmann
King's College London
Dept. of Chemistry
London, WC2R 2LS
UK
tel: 44 171 873-2767
fax: 44 171 873-2810
J.Altmann@kcl.ac.uk

Dr. Wayne Anderson
Bloomsburg University
Dept. of Chemistry
Bloomsburg, PA 17815
USA
tel: 1 717 389-4146
fax:
wpa@planetx.bloomu.edu

Ms. Iris Antes
Universitaet Zuerich
Winterthurerstr. 190
Zuerich, 8057
Switzerland
tel: 41 1 635-6119
fax:
antes@oci.unizh.ch

Dr. Gustavo Arteca
Laurentian University
Dept. of Chemistry
Ramsey Lake Road
Sudbury, ON P3E 2C6
Canada
tel: 1 705 675-1151
fax: 1 705 675-4844
Gustavo@nickel.laurentian.ca

Prof. Vikiorya Aviyente
Bogazici University
Department of Chemistry
Bebek
Istanbul, 80815
Turkey
tel: 90 212 263-1540
fax: 90 212 287-2467

Mr. Pradipta Bandyopadhyay
Institute for Molecular Sciences
Nishigo-naka 38, Myodaiji
Okazaki, Aichi 444-8585
Japan
tel: 81 564 55-7261
fax: 81 564 53-4660
pradipta@ims.ac.jp

Dr. Roman Baranowski
University of British Columbia
Department of Chemistry
2036 Mail Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6549
fax: 1 604 822-2847
roman@chem.ubc.ca

Prof. Axel Becke
Queen's University
Dept. of Chemistry
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-2634
fax: 1 613 545-6669
becke@chem.queensu.ca

Prof. Gert D. Billing
University of Copenhagen
Dept. of Chemistry
Universitets parkin 5
Copenhagen, 2100
Denmark
tel: 453 532 0252
fax: 453 532 0759
gdb@maldyn.ki.ku.dk

Dr. Peter E. Blochl
IBM Zurich Research Laboratory
Saumerstr. 4
Ruschlikon, CH-8803
Switzerland
tel: 411 724-8656
fax: 411 724-8958
blo@zurich.ibm.com

Mr. David Block
University of Calgary
Dept. of Chemistry
Calgary, Ab T2N 1N4
Canada
tel: 1 403 220-6905
fax: 1 403 289-9488
dablock@chem.ucalgary.ca

Mr. Russell J. Boyd
Dalhousie University
Department of Chemistry
Halifax, NS B3H 4J3
Canada
tel: 1 902 494-3709
fax: 1 902 494-1310

Prof. Dilek Calgan
Bogazici University
Department of Chemistry
Bebek
Istanbul, 80815
Turkey
tel: 90 212 2631540 x1671
fax: 90 212 2872467
calgan@boun.edu.tr

Miss Irina Calugareanu
Queen's University
Dept. of Chemistry
Frost Wing
Kingston, ON K7L 3N6
Canada
tel: 1 613 531-3947
fax: 1 613 545-6669
irina@chem.queensu.ca

Dr. Dale Cameron
Bio-Mega
Dept. of Chemistry
2100 Cunard Street
Laval, PQ H7S 2G5
Canada
tel: 1 450 682-4640
fax: 1 450 682-4189
dcameron@bio-mega.boehringer-ingelheim.ca

Dr. Roberto Cammi
Universita di Parma
Chimica Generale eol Inorganila
Viale delle Scienze, 1
Parma, I-43100
Italy
tel: 39 521 905-442
fax: 39 521 905-557

Dr. Philip Camp
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6262
fax: 1 604 822-2847
philip@theory.chem.ubc.ca

Prof. Natalie Cann
Queen's University
Dept. of Chemistry
Frost Building, Room 515
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-2651
fax: 1 613 545-6669
ncann@chem.queensu.ca

Dr. Ian Carmichael
Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556
USA
tel: 1 219 631-4502
fax: 1 219 631-8068

Prof. Emily Carter
University of California, Los Angeles
Dept. of Chemistry and Biochemistry
Box 951569
Los Angeles, CA 90095-1569
USA
tel: 1 310 206-5118
fax: 1 310 206-4038
eac@chem.ucla.edu

Dr. Mark E. Casida
Universite de Montreal
Dept. of Chemistry
C.P. 6128, Succ. Centre-ville
Montreal, PQ H3C 3J7
Canada
tel: 1 514 343-6111 x3901
fax: 1 514 343-2468

Dr. Cary Chabalowski
US Army Research Laboratory
AMSRL-WM-BD
Aberdeen Proving Ground, MD 21005-5066
USA
tel: 1 410 278-6095
fax: 1 410 278-6150
cary@arl.mil

Miss Heli Chen
University of British Columbia
121-1984 Mathematics Rd.
Vancouver, BC V6T 1Z2
Canada
tel: 1 604 822-4876
fax:
hchen@math.ubc.ca

Prof. Zekiye Cinar
Yildia Techical University
Department of Chemistry
Istanbul, 80270
Turkey
tel: 90 212 224-5000
fax: 90 216 348-6652

Dr. John Cullen
University of Manitoba
Dept. of Chemistry
350 Parker Bldg.
Winnipeg, MB R3T 2N2
Canada
tel: 1 204 474-6441
fax: 1 204 474-7605
cullen@cc.umanitoba.ca

Mr. Bedamati Das
Queen's University
Dept. of Chemistry
Frost Wing Room 511
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-6000 x7862
fax:
bedamati@chem.queensu.ca

Mr. Tyler Day
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6262
fax: 1 604 822-2847
day@theory.chem.ubc.ca

Dr. Dominique Dehareng
University of Liege
Centre d'Ingenierie des Proteines
Institut de Chimie B6, Sart Tilman
Leige, B4000
Belgium
tel: 3243 663499
fax: 3243 663364
d.dehareng@ulg.ac.be

Dr. Tom Dingle
University of Victoria
Dept. of Chemistry
Box 3065
Victoria, BC V8L 1J4
Canada
tel: 1 250 721-7162
fax: 1 250 721-7147
chemgrad@uvvm.uvic.ca

Dr. Georges Dive
University of Liege
Centre d'Ingenierie des Proteines
Institut de Chimie B6, Sart Tilman
Leige, B4000
Belgium
tel: 3243 663499
fax: 3243 663364
gdive@ulg.ac.be

Dr. David Dixon
PNNL
906 Battelle Blvd.
MS K1-83
Richland, WA 99352
USA
tel: 1 509 372-4999
fax: 1 509 375-6631
david.dixon@pnl.gov

Mr. Robert Doerksen
University of New Brunswick
Dept. of Chemistry
Fredericton, NB E3B 6E2
Canada
tel: 1 506 453-4781
fax: 1 506 453-4981
K3LZ@unb.ca

Mr. Albrecht Dokalik
University of Vienna
Dept. of Organic Chemistry
Wahringerstrasse 38
Vienna, 1090
Austria
tel: 43 1 31367 2304
fax: 43 1 37367 2280
aldo@felix.orc.univic.ac.at

Dr. Ken Dyall
Thermosciences Institute
NASA Ames Research Center
Mail Stop 230-3
Moffett Field, CA 94035-1000
USA
tel: 1 650 604-6361
fax: 1 650 604-0350
dyall@pegasus.arc.nasa.gov

Dr. Allan East
NRC
Steacie Inst. for Mol. Sciences
100 Sussex
Ottawa, ON K1A 0R6
Canada
tel: 1 613 991-9865
fax: 1 613 947-2838
allan.east@nrc.ca

Dr. Paul F. Endres
Bowling Green State University
Dept. of Chemistry
Bowling Green, OH 43403
USA
tel: 1 419 372-8744
fax:
endres@opie.bgsu.edu

Dr. Eliav Ephraim
Tel Aviv University
School of Chemistry
Ramat-Aviv
Tel Aviv, 69978
Israel
tel: 972 3 640-7634
fax: 972 3 640-9293
ephraim@chemib6.tau.ac.il

Dr. Martin Field
IBS
Dept. LDM
41 Avenue des Martyrs
Grenoble, Cedex 1 38027
France
tel: 33 476 88-9594
fax: 33 476 88-5494
mjfield@ibc.fr

Dr. Srinivas Gantasala
University of Alabama
Dept. of Chemistry
901, 14th Street So.
Birmingham, AL 35294
USA
tel: 1 205 934-8161
fax: 1 205 934-8955
naga@picasso.chem.uab.edu

Prof. Jiali Gao
SUNY Buffalo
Dept. of Chemistry
Natural Sciences & Mathematics Complex
Buffalo, NY 14260
USA
tel: 1 716 645-6800 x2102
fax: 1 716 645-6963
jiali@chem.buffalo.edu

Dr. James Gauld
Uppsala University
Dept. of Quantum Chemistry
BOX 518
Uppsala, s-751 20
Sweden
tel: 011 46 18 471-3269
fax: 011 46 18 502402
james@kvac.uu.se

Mr. German Gavigliasso
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6549
fax: 1 604 822-0614
germanec@chem.ubc.ca

Prof. John D. Goddard
University of Guelph
Dept. of Chemistry & Biochemistry
Guelph, ON N1G 2W1
Canada
tel: 1 419 824-4120 x3061
fax: 1 519 766-1499
goddard@chembio.uoguelph.ca

Prof. Mark Gordon
Iowa State University
201 Spedding Hall
Ames, IA 50011
USA
tel: 1 515 294-0452
fax: 1 515 294-5204
mark@si.fi.ameslab.gov

Mr. Andrei Goryachev
University of Toronto
Dept. of Chemistry
80 St. George St.
Toronto, ON M5S 3H6
Canada
tel: 1 416 978-6191
fax: 1 416 978-5325
agoryach@gatto.chem.utoronto.ca

Prof. Fritz Grein
University of New Brunswick
Dept. of Chemistry
Fredericton, NB E3B 6E2
Canada
tel: 1 506 453-4776
fax: 1 506 453-4981
fritz@unb.ca

Prof. John Gunn
Universite de Montreal
Dept. of Chemistry
C.P. 6128, Succ. Centre-ville
Montreal, PQ H3C 3J7
Canada
tel: 1 514 343-7636
fax: 1 514 343-7586
gunnj@cerca.umontreal.ca

Dr. Maciej Gutowski
Pacific Northwest National Laboratory
Materials and Chemical Sciences
P.O. Box 999/MS K2-18
Richland, WA 99352
USA
tel: 1 509 375-4387
fax: 1 509 375-2167
ms_gutowski@pnl.gov

Dr. Tracy Hamilton
UAB
Dept. of Chemistry
Birmingham, AL 35294-1240
USA
tel: 1 205 934-8956
fax: 1 205 934-8955
hamilton@uab.edu

Prof. Nicholas Handy
University of Cambridge
Dept. of Chemistry
Lensfield Road
Cambridge, Cambs CB2 1EW
UK
tel: 011 44 1223 336373
fax: 011 44 1223 336362
nch1@cam.ac.uk

Miss. Arzu Hatipoglu
Yildia Techical University
Department of Chemistry
Istanbul, 80270
Turkey
tel: 90 212 224-5000
fax: 90 216 348-6652

Prof. John Head
University of Hawaii
Dept. of Chemistry
2545 The Mall
Honolulu, Hawaii 96822
USA
tel: 1 808 956-5787
fax: 1 808 956-5908

Prof. Martin Head-Gordon
U.C. Berkeley
419 Latimer Hall
Berkeley, CA 94720
USA
tel: 1 510 643-2816
fax: 1 510 643-6232
sonja@cchem.berkeley.edu

Mr. So Hirata
The Graduate University for Advanced Studie
Nishigo-naka 38, Myodaiji
Okazaki, Aichi 444-8585
Japan
tel: 81 564 55-7261
fax: 81 564 53-4660
soh@ims.ac.jp

Dr. Margaret Hurley
Ohio Supercomputer Center
939-1 Beards Hill Rd. Suite 193
Aberdeen, MD 21001
USA
tel: 1 410 297-8568
fax: 1 410 297-9521
hurley@osc.edu

Mr. Toshimasa Ishida
Shikuoka University
Faculty of Engineering(Common Education
836 Ohya
Shizuoka, 422-8529
Japan
tel: 81 54 238-4933
fax: 81 54 238 4933
ishida-t@eng.shizuoka.ac.jp

Prof. Yasuyuki Ishikawa
University of Puerto Rico
Dept. of Chemistry
P.O. Box 23346
San Juan, Puerto Rico 00931-3346
USA
tel: 1 787-764-0000
fax: 1 787 751-0625
ishikawa@rrpac.upr.clu.edu

Prof. Swehiro Iwata
Institute for Molecular Sciences
Theor. Division I
Okazaki,
Japan
tel: 81 564 557300
fax: 81 564 534660
iwata@ims.ac.jp

Prof. David Jack
Concordia University
Dept. of Chemistry
1455 de Maisionneuve Blvd. W.
Montreal, PQ H3G 1M8
Canada
tel: 1 514 848-3387
fax: 1 514 848-2868
david@planck.concordia.ca

Dr. Dylan Jayatilaka
University of Western Australia
Nedlands, WA 6009
Australia
tel: 61 08 9380 3515
fax: 61 08 9380 1005
dylan@crystal.uwa.edu.au

Dr. Dan Jonsson
San Diego Supercomputer Centre
9500 Gilman Drive, MC 0505
La Jolla, CA 92093-0505
USA
tel: 1 916 822-0916
fax: 1 916 534-5117
dajon@sdsc.edu

Prof. Uzi Kaldor
Tel Aviv University
School of Chemistry
Tel Aviv, 69978
Israel
tel: 972 3 640 8590
fax: 972 3 640 9293
kaldor@jade.tau.ac.il

Prof. Kenneth Kay
Bar-Ilan University
Dept. of Chemistry
Ramat-Gan, 52900
Israel
tel: 972 3 531-8722
fax: 972 3 535-1250
kay@mail.biu.ac.il

Prof. Masahiro Kinoshita
Kyoto University
Institute of Advanced Energy
Uji-shi, Kyoto-fu 611-0011
Japan
tel: 81 774 38-3503
fax: 81 774 38-3508
kinoshita@iae.kyoto-u.ac.jp

Dr. Elise Kochanski
CNRS and ULP
UMR 7551, Lab.Chimie, Quantique et Chimie
Institute Le Bel, Universite Louis Pasteur, BP 2
Strasbourg, 67008
France
tel: 33 0388 416-108
fax: 33 0388 612-085
kochanski@quantix.u_strasbg.fr

Dr. Tamiki Komatsuzaki
The University of Chicago
Dept. of Chemistry
5735 S. Ellis Avenue
Chicago, IL 60637
USA
tel: 1 773 702-7052
fax: 1 773 702-0805
tamiki@cloister.uchicago.edu

Dr. Morris Krauss
Centre for Advanced Research Biotechnology
9600 Gudelsky Drive
Rockville, MD 20850
USA
tel: 1 301 738-6242
fax: 1 301 738-6255

Dr. Peter Kusalik
Dalhousie University
Department of Chemistry
Halifax, NS B3H 4J3
Canada
tel: 1 902 494-3627
fax: 1 902 494-1310
kusalik@is.dal.ca

Dr. Nancy Lamontagne
NIH
CSR
Room 4170, 6701 Rockledge Drive
Bethesda, MD 20892
USA
tel: 1 301 435-1726
fax: 1 301 480-2327
LAMONTAN@dry.nih.gov

Dr. Jerzy Leszczynski
Jackson State University
Dept. of Chemistry
1400 J.R. Lynch Street, PO Box 17910
Jackson, MI 39217
USA
tel: 1 601 973-3723
fax: 1 601 973-3674
jerzy@tiger.jsums.edu

Dr. Zhifeng Liu
Chinese University of Hong Kong
Dept. of Chemistry
Shatin
Hong Kong,
P.R. China
tel: 852 2609-6358
fax: 852 2603-5057
zfliu@cuhk.edu.hk

Prof. Lawrence Lohr
University of Michigan
Dept. of Chemistry
Ann Arbor, MI 48109-1055
USA
tel: 1 734 764-3148
fax: 1 734 647-4865
llohr@umich.edu

Dr. Gerald Lushington
Ohio Supercomputer Center
1224 Kinnear Road
Columbus, OH 43212-1163
USA
tel: 1 614 292-6036
fax: 1 614 292-7168
gerald@osc.edu

Prof. Robert Maclagan
University of Canterbury
Dept. of Chemistry
Private Bag 4800
Christchurch,
New Zealand
tel: 643 361-2456
fax: 643 264-2110
r.maclagan@chem.canterbury.ac.nz

Dr. Jaime Martell
Lyon College
2300 Highland Drive
Batesville, AR 72503-2317
USA
tel: 1 870 698-4688
fax: 1 870 698-4622
jmartell@lyon.edu

Prof. Joao Martins
UNESP - Bauru
Faculdade de Ciencias
Departamento de Quimica
Bauru, Sao Paulo 17033-360
Brazil
tel: 55 14 230-2111
fax: 55 14 230-9386
lopes@cat.cbpf.br

Prof. Hidenori Matsuzawa
Chiba Institute of Technology
Dept. of Chemistry
2-1-1 Shibazono
Narashino, Chiba 275-0023
Japan
tel: 81 474 54-9602
fax: 81 474 54-9602
matuzawa@cc.it-chiba.ac.jp

Prof. Fred McCourt
University of Waterloo
Dept. of Chemistry
200 University Avenue West
Waterloo, ON N2L 3G1
Canada
tel: 1 519 888-4567 x3024
fax: 1 519 746-0435
MCCOURT@THEOCHEM.UWATERLOO.CA

Mr. James McWhirter
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6262
fax: 1 604 822-2847

Dr. Alexander Mebel
Institute of Atomic and Molecular Sciences
Academia Sinica
P.O. Box 23-166
Taipai, 10764
Taiwan
tel: 886 22366-8208
fax: 886 22362-0200
mebel@po.iams.sinica.edu.tw

Dr. Anthony J.H.M. Meijer
Wayne State University
Dept. of Chemistry
Detroit, MI 48202
USA
tel: 1 313 577-2550
fax: 1 313 577-8822
anthony@dynamo.chem.wayne.edu

Prof. Wilfried Meyer
University of Kaiserslautern
Dept. of Chemistry
Erwin-Schrodinger-Str.
Kaiserslautern, 67663
Germany
tel: 49 631 205-2581
fax: 49 631 205-2187
meyer@chemie.uni-kl.de

Prof. Werner Mikenda
University Vienna
Inst. Org. Chem.
Wahringerstrasse 38
Vienna, A-1090
Austria
tel: 431 313 67 2209
fax: 431 313 67 2280
WERNER.MIKENDA@UNIVIE.AC.AT

Dr. Eduardo E. Mola
Faculty of Sciences - Chemistry
Casilla de Correo 314
La Plata, 1900
Argentina
tel: 54 1 202-2403
fax: 54 2 125-4642
eemola@inifta.edu.ar

Prof. Keiji Morokuma
Emory University
Dept. of Chemistry
1515 Pierce Drive
Atlanta, GA 30322
USA
tel: 1 404 727-2180
fax: 1 404 727-6586
morokuma@emory.edu

Dr. Richard Moss
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6262
fax:
rjm@seymour.chem.ubc.ca

Mr. Baik Mu-Hyun
University of North Carolina, Chapel Hill
Dept. of Chemistry
CB #3290, Venable Hall
Chapel Hill, NC
USA
tel:
fax:
publishr@yoda.chem.unc.edu

Dr. Heidi M. Muchall
McMaster University
Dept. of Chemistry
Hamilton, ON L8S 4M1
Canada
tel: 1 905 525-9140
fax: 1 905 522-2509
MUCHALL@MCMASTER.CA

Prof. Hiroshi Nakatsuji
Kyoto University
Dept. of Synthetic Chemistry and Biological
Sakyo-ku, Yoshida
Kyoto, 606-8501
Japan
tel: 81 75 753-5653
fax: 81 75 753-5910
hiroshi@sbchem.kyoto-u.ac.jp

Dr. Duncan Napier
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6549
fax:

Mr. Nam-Ah Nguyen
Universite Laval
Departement de chimie
Quebec, PQ G1K 7P4
Canada
tel: 1 418 656-2131 x4798
fax: 1 418 656-7916
anh@chm.ulaval.ca

Prof. Tung Nguyen-Dang
Universite Laval
Departement de chimie
Quebec, PQ G1K 7P4
Canada
tel: 1 418 656-3853
fax: 1 418 656-7916
tung@chm.ulaval.ca

Dr. Andreas Nicklass
Washington State University
Pacific Northwest National Laboratory
PO Box 999, MSIN K1-96
Richland, WA 99352
USA
tel: 1 509 372-4897
fax:
Andreas.Nicklass@pnl.gov

Mr. Steve Nielsen
University of Toronto
Dept. of Chemistry - Chemical Physics Theory
80 St. George St.
Toronto, ON M5S 3H6
Canada
tel: 1 416 978-5325
fax: 1 416 978-5325
snielsen@gatto.chem.utoronto.ca

Miss. A. Neren Okte
Bogazici University
Department of Chemistry
FEF Kimya Bolumu ARS.Gor
Bebek/Istanbul, 80815
Turkey
tel: 90 212 263-1540X1610
fax: 90 212 287-2467

Mr. Luis Ortiz
Engineering Institute
Mech. Thermal and Fluids Eng.
Avenida Universidad 1923 No. D-302 Torres d
Mexico D.F., Oxtopulco Univ. 04310
Mexico
tel: 525 661-3943
fax: 525 616-1514
lao@hidros.iingen.unam.mx

Dr. Vincent Ortiz
Kansas State University
Dept. of Chemistry
111 Willard Hall
Manhattan, K 66506-3701
USA
tel: 1 785 532-6071
fax: 1 785 532-6666
ortiz@ksu.edu

Mr. Frank Otto
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-6262
fax:
OTTO@THEORY.CHEM.UBC.CA

Prof. Ourida Ouamerali
USTUB - Dept. of Chemistry
Lab de Physicochimie Quantique USTHB
Alger, Babezzouar 16111
Algeria
tel: 011 213 251 5575
fax: 011 213 251 5217
ouamerali@ist.cerist.dt

Mr. Jeff Paci
Queen's University
Dept. of Chemistry
Frost Wing Room 511
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-6413
fax: 1 613 545-6669
jpaci@chem.queensu.ca

Prof. Guiseppe C. Pappalardo
Universita di Cantania
Dipartimento Scienzechii
Viale A. Doria, 6
Cantania, T-95125
Italy
tel: 3995 33751
fax: 3995 580138
GCPAPPALARDO@DIPCHI.UNICT.IT

Dr. Serguei Patchkovskii
University of Calgary
Dept. of Chemistry
2500 University Drive N.W.
Calgary, Ab T2N 1N4
Canada
tel: 1 403 220-7176
fax: 1 403 289-9488
patchkov@acs.ucalgary.ca

Dr. Gren Patey
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-2996
fax:
patey@theory.chem.ubc.ca

Mr. Jerome K. Percus
New York University
Courant Institute and Physics Department
251 Mercer Street
New York, NY 10012
USA
tel:
fax:

Dr. Joakim Persson
National Supercomputer Centre
Linkoping University
Linkoping, 58183
Sweden
tel: 4613 285797
fax: 4613 282535
bjp@nsc.liu.se

Mr. Laurent Petitjean
Groupement de Recherche de Lacq
Service Chemie-Physique
BP 34
ARTIX, 64170
France
tel: 335 59 92 6734
fax: 335 59 92 6765

Prof. Monte Pettitt
University of Houston
Dept. of Chemistry
Houston, TX 77204-5641
USA
tel: 1 713 743-3263
fax: 1 713 743-2709
pettitt@uh.edu

Dr. Jose Pires
The University of Calgary
3330 Hospital Drive
Calgary, AB T2N 4N1
Canada
tel: 1 403 220-3059
fax: 1 403 270-0979
pires@acs.ucalgary.ca

Dr. Vladimir Pitchko
University of Western Ontario
Dept. of Chemistry
London, ON N6A 5B7
Canada
tel: 1 519 679-2111 x6351
fax: 1 519 661-3022
vpitchko@julian.uwo.ca

Dr. Robert Polly
San Diego Supercomputer Center
University of California, San Diego, MC 0505
9500 Gilman Drive, Building 109
La Jolla, CA 92093
USA
tel: 1 619 534-8323
fax: 1 619 534-5113
pollu@sdsc.edu

Mr. James Polson
FOM Institute for Atomic and Molecular Physics
Kruislaan 407
SJ, 1098
Amsterdam
tel: 31 20 608-1228
fax: 31 20 668-4106
polson@amolf.nl

Dr. Cory Pye
University of Calgary
Dept. of Chemistry
2500 University Drive NW
Calgary, Ab T2N 1N4
Canada
tel: 1 403 220-3232
fax: 1 403 289-9488

Prof. Susanne Raynor
Rutgers University
Dept. of Chemistry
Newark, NJ 07102
USA
tel: 1 973 353-5041
fax: 1 973 353-1264
sraynor@andromeda.rutgers.edu

Prof. William Reinhart
University of Washington
Dept. of Chemisty
Box 351700
Seattle, WA 98195-1700
USA
tel: 1 206 543-0578
fax: 1 206 685-8665
rein@chem.washinton.edu

Prof. Jean-Louis Rivail
University Henri-Poincare
B.P. 239
Nancy-Vandoeuvre, 54506
France
tel: 33 383 91-2379
fax: 33 383 91-2530
Jean-Louis.Rivail@lctn.u-nancy.fr

Prof. Michael Robb
King's College London
Strand
London, WC2R 2LS
UK
tel: 44 171 873-2098
fax: 44 171 873-2810
mike.robb@kcl.ac.uk

Prof. David Ronis
McGill University
Chemistry Dept.
810 Sherbrooke Street West
Montreal, PQ H3A 2K6
Canada
tel: 1 514 398-5099
fax: 1 514 398-3797
ronis@onsager.chem.mcgill.ca

Dr. Pierre-Nicholas Roy
Voth Group
Chemistry Department
University of Utah
Salt Lake City, Utah 84112
USA
tel: 1 801 581-8606
fax: 1 801 581-4353
pnroy@hec.utah.edu

Dr. Safiye Sag Erdem
Bogazici University
Department of Chemistry
Bebek
Istanbul, 80815
Turkey
tel: 90 212 263-1540
fax: 90 212 287-2467

Prof. Shogo Sakai
Osaka Sangyo University
Information Systems Engineering
Nakagaito 3-1
Daito, Osaka
Japan
tel: 817 2089 2538
fax: 817 2089 2539

Dr. Dennis Saluhub
Universite de Montreal
Dept. of Chemistry
C.P. 6128, Succ. Centre-ville
Montreal, PQ H3C 3J7
Canada
tel: 1 514 343-6755
fax: 1 514 343-2468
Dennis.Saluhub@umontreal.ca

Prof. Lothar Schafer
University of Arkansas
Department of Chemistry
Fayetteville, AR 72701
USA
tel: 1 501 575-5079
fax: 1 501 575-4049
schafer@soilchem.uark.edu

Dr. Rockus Schmid
University of Calgary
Dept. of Chemistry
2500 University Drive NW
Calgary, Ab T2N 1N4
Canada
tel: 1 403 220-3232
fax:
rschmid@acs.ucalgary.ca

Dr. Hartmut L. Schmider
Queen's University
Dept. of Chemistry
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-2647
fax: 1 613 545-6669
hasch@ct3a.chem.queensu.ca

Prof. Jeremy Schofield
University of Toronto
Dept. of Chemistry
80 St. George St.
Toronto, ON M5S 3H6
Canada
tel: 1 416 978-4376
fax: 1 416 978-8775
jmschofi@chem.utoronto.ca

Dr. Georg Schreckenbach
Los Alamos National Lab
T-12
MS B268
Los Alamos, NM 87545
USA
tel: 1 505 667-7605
fax: 1 505 665-3909
schrecke2t12.lanl.gov

Prof. Gustavo Scuseria
Rice University
Dept. of Chemistry
6100 Main Street - MS 60
Houston, TX 77005-1892
USA
tel: 1 713 527-4746
fax: 1 713 285-5155
guscus@katzo.rice.edu

Prof. Tamar Seideman
Steacie Institute
National Research Council
100 Sussex Drive
Ottawa, ON K1A 0R6
Canada
tel: 1 613 990-0945
fax: 1 613 947-2838
tamar.seideman@nrc.ca

Mr. Michael Seidl
Tulane University
Dept. of Physics
New Orleans, LA 70118
USA
tel: 1 504 862-3173
fax: 1 504 862-8702
michael@mailhost.tcs.tulane.edu

Mr. Cenk Selcuki
Bogazici University
Department of Chemistry
Bebek
Istanbul, 80815
Turkey
tel: 90 212 263-1540x1610
fax: 90 212 287-2467
selcuki@boun.edu.tr

Dr. Irene Shim
Technical University of Denmark
Applied Chemistry
DTU 375
Lyngby, DK 2800
Denmark
tel: 45 45 255432
fax: 45 45 886138
itakis@pop.dtu.dk

Prof. Bernie D. Shizgal
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-3997
fax: 1 604 822-2847
shizgal@theory.chem.ubc.ca

Dr. Willem Siebrand
NRC
SIMS
Ottawa, ON K1A 0R6
Canada
tel: 1 613 990-0968
fax: 1 613 947-2838
willem.siebrand@nrc.ca

Mr. Per Siegbahn
Stockholm University
Dept. of Physics
Box 6730, S-11385
Stockholm,
Sweden
tel: 46 816-4621
fax: 46 834-7817
ps@physto.se

Ms. Alexandra Simperler
University of Vienna
Dept. of Organic Chemistry
Wahringerstrasse 38
Vienna, 1090
Austria
tel: 431 313 67-2287
fax: 431 313 67-2280
alex@felix.orc.univie.ac.at

Mr. Vedene Smith
Queen's University
Dept. of Chemistry
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-2650
fax: 1 613 545-6669
vhsmith@chem.QueensU.ca

Prof. Robert Snider
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-2537
fax: 1 604 822-2847
snider@theory.chem.ubc.ca

Prof. Jaap G. Snijders
University of Groningen
Material Science Centre
Nyenborgh 4
Groningen, 9747 AG
The Netherlands
tel: 31 50 3634861
fax: 31 50 3634447
SNIJDERS@CHEM.RUG.NL

Dr. Humberto Soscun
La Universidad del Zulio
Facultad de Ciencias, Departamento de Quimica
Grano de oro. Modulo #2
Maracaibo, Zulia 526
Venezuela
tel: 58 61 317-902
fax: 58 61 311-348
humbero@sinamaica.ciens.luz.ve

Dr. Ming-Der Su
National Tsing Hua University
Dept. of Chemistry
Hsinchu, Taiwan 30043
R.O.C.
tel: 886 35 715131 x3389
fax: 886 35 711082
ggs@chul.chem.nthu.edu.tw

Prof. Dage Sundholm
University of Helsinki
Department of Chemistry
P.O. Box 55 (A.I. Virtasen aukio 1)
Helsinki, FIN-00014
Finland
tel: 358 9 1914-0176
fax: 358 9 1914-0469
Sundholm@Chem.Helsinki.Fi

Mr. Kudo Takako
Gunma University
1-5-1 Tenjin-cho
Kiryu, Gunma-Prefecture 376-8515
Japan
tel: 812 7730 1935
fax: 812 7740 1026
tkudo@ns518.eg.gunma-u.ac.jp

Prof. Keiko Takano
Ochanomizu University
Dept. of Chemistry, Faculty of Science
2-1-1 Otsuka, Bunkyo-ku
Tokyo, 112-8610
Japan
tel: 813 5978 5338
fax: 813 5978 5335
keiko@chem.ocha.ac.jo

Mr. Fu-Ming Tao
California State University, Fullerton
Dept. of Chemistry & Biochemistry
800 North State College Blvd.
Fullerton, CA 92834
USA
tel: 1 714 278-4517
fax: 1 714 278-4663
ftao@fullerton.edu

Dr. Mark Thachuk
University of British Columbia
Department of Chemistry
2036 Main Mall
Vancouver, BC V6T 1Z1
Canada
tel: 1 604 822-2448
fax: 1 604 822-2847
thachuk@chem.ubc.ca

Dr. Ajit Thakkar
University of New Brunswick
Dept. of Chemistry
Fredericton, NB E3B 6E2
Canada
tel: 1 506 453-4629
fax: 1 506 453-4981
ajit@unb.ca

Dr. Hiroaki Tokiwa
Rikkyo University
3-34-1 Nishi-Ikebukuro
Toshima-ku
Tokyo, 171-8501
Japan
tel: 81 3 3985-2394
fax: 81 3 5992-3434
tokiwa@chem.rikkyo.ac.jp

Prof. Alejandro Toro-Labbe
Deptamento de Quimica Fisica
Pontificia Universidad Catolica de Chile
Casilla 306, Correo 22
Santiago,
Chile
tel: 56 2 686-4746
fax: 56 2 686-4744
atola@puc.cl

Prof. Glenn Torrie
Royal Military College
Dept. of Chemistry and Chemical Engineering
P.O. Box 17000 Station Forces
Kingston, ON
Canada
tel: 1 613 541-6000 x6476
fax: 1 613 542-9489
torrie-g@rmc.ca

Mr. John Tse
National Research Council of Canada
Steacie Institute of Molecular Sciences
100 Sussex Drive
Ottawa, ON K1A 0R6
Canada
tel: 1 613 991-1237
fax:
tse@ned1.sims.nrc.ca

Dr. Eric Turner
Northwest Community College
Dept. of Physics
5331 McConnell Avenue
Terrace, BC V8G 4C2
Canada
tel: 1 250 635-2700
fax:
TURNER@NWCC.BC.CA

Dr. Kentaro Uehara
National Research Council of Canada
100 Sussex Drive
Ottawa, ON K1A 0R6
Canada
tel: 1 613 993-7966
fax: 1 613 947-2838
uehara@ned1.sims.nrc.ca

Prof. Luc Vanquickenborne
University of Leuven
Chemistry Department
Celestijnenlaan 200F
Heverlee-Leuven, B-3001
Belgium
tel: 32 16 327359
fax: 32 16 327992
luc.vanquickborne@chem.kuleuven.ac.be

Prof. Tereza Varnali
Bogazici University
Department of Chemistry
Bebek
Istanbul, 80815
Turkey
tel: 90 212 263-1540x1815
fax: 90 212 287-2467
varnali@boun.edu.tr

Prof. Greg Voth
University of Utah
Department of Chemistry
315 S. 1400 E.Rm Dock
Salt Lake City, Utah 84112
USA
tel: 1 801 581-7272
fax: 1 801 581-4353
voth@chemistry.chem.utah.edu

Dr. Richard Wang
Dalhousie University
Department of Physics
Halifax, NS B3H 3J5
Canada
tel: 1 902 494-6594
fax: 1 902 494-5191
wang@is.dal.ca

Prof. David Wardlaw
Queen's University
Dept. of Chemistry
Kingston, ON K7L 3N6
Canada
tel: 1 613 545-2632
fax: 1 613 545-6669
david@chem.queensu.ca

Prof. Michel Waroquier
University of Gent
Department of Theoretical Physics
Proftuinstraat, 86
Gent, Oost-Vlaanderen, B-9000
Belgium
tel: 32 9 264-6542
fax: 32 9 264-6699
michel@inwfaxp2.rug.ac.be

Prof. Ariel Warshel
University of Southern California
Department of Chemistry
University Park
Los Angeles, CA 90089
USA
tel: 1 213 740-4114
fax:

Dr. Noham Weinberg
Simon Fraser University
Dept. of Chemistry
Burnaby, BC V5A 1S6
Canada
tel: 1 604 291-5627
fax: 1 604 291-3765
weinberg@sfu.ca

Ms. Stacey D. Wetmore
Dalhousie University
Department of Chemistry
Halifax, NS B3H 4J3
Canada
tel: 1 902 494-7021
fax: 1 902 494-1310
swetmore@is2.dal.ca

Mr. Michael A. Whitehead
McGill University
Chemistry Dept.
801 Sherbrooke Street West
Montreal, PQ H3A 2K6
Canada
tel: 1 514 398-6239
fax: 1 514 398-3797
tony@maw.chem.mcgill.ca

Dr. Joshua Wilkie
Northwestern University
Dept. of Chemistry
2145 N. Sheridan Road
Evanston, IL 60208-3113
USA
tel: 1 847 491-7189
fax: 1 847 491-7713
jwilkie@chem.nwu.edu

Dr. Stephen Wolff
University of Calgary
2500 University Drive N.W.
Calgary, AB T2N 1N4
Canada
tel: 1 403 220-8204
fax: 1 403 289-9488
swolff@acs.ucalgary.ca

Dr. James S. Wright
Carleton University
Dept. of Chemistry
1125 Colonel By Drive
Ottawa, ON K1S 5B6
Canada
tel: 1 613 520-3645
fax: 1 613 520-3749
jim_wright@carleton.ca

Mr. Akira Yoshimori
Kyushu University
Department of Physics
Ropponmatsu
Fukonka, 810-8560
Japan
tel: 81 92 726-4767
fax:
yoshimori@rc.kyushu-u.ac.jp

Prof. Tom Ziegler
University of Calgary
Department of Chemistry
2500 University Drive
Calgary, AB T2N 1N4
Canada
tel: 1 403 220-5368
fax: 1 403 289-9488
ziegler@zinc.chem.ucalgary.ca